

Gold-Catalyzed Cyanosilylation Reaction: Homogeneous and Heterogeneous Pathways

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Abstract: Gold had been considered to be an extremely inert metal, but recently it was found that nanometer-sized gold particles on metal-oxide supports acted as catalysts for simple organic reactions, such as oxidation and hydrogenation, even at or below room temperature. Herein, we report that gold nanoparticles (AuNPs) of zero oxidation state (Au⁰) are catalytically active for a C–C bond-forming reaction, the cyanosilylation of aldehydes. The AuNP-catalyzed cyanosilylation

proceeded smoothly at room temperature with 0.2 wt% loading of AuNPs. The reactions of aromatic aldehydes were almost quantitative, except for benzaldehyde derivatives containing the electron-withdrawing NO₂ group, and α,β -unsaturated aromatic aldehydes were the most reactive sub-

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strates. The reactions also went smoothly for aliphatic aldehydes. Mechanistic studies indicated that the reactions proceeded both homogeneously and heterogeneously: homogeneous catalysis by leached gold species and heterogeneous catalysis by the adsorption of the reactants (aldehydes and trimethylsilyl cyanide) onto AuNPs. The ratio of homogeneous and heterogeneous catalysis was estimated to be $\approx 4:1$.

Introduction

Gold is one of the least reactive metals, and has long been considered as a poorly active catalyst. However, recently there have been a growing number of reports that gold nanoparticles (AuNPs), especially metal-oxide-supported AuNPs, can serve as very efficient catalysts. Among the reported reactions, the most famous example is the AuNP-catalyzed CO oxidation^[1] at very low temperature. This reaction has attracted great attention experimentally and theoretically because it has commercial value. The Pt/Pd catalysts that are currently used in cars for CO oxidation work only at temperatures above 200 °C. Therefore, CO pollution is unavoidable during the first five minutes after starting the engine. This problem can clearly be solved by low-tempera-

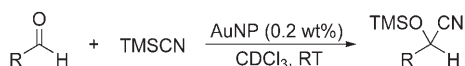
ture, AuNP-catalyzed CO oxidation.^[2] Since the discovery that metal-oxide-supported AuNPs were catalytically active for CO oxidation, the scope of AuNP-catalyzed reactions has been expanded to other reactions, such as selective oxidation of alcohols,^[3] epoxidation of propene,^[4] NO reduction with O₂ and H₂,^[5] selective oxidation of cyclohexene,^[6] hydrogenation of unsaturated hydrocarbons,^[7] the water–gas shift reaction,^[8] and formation of carbodiimide between isocyanide and primary amines.^[9] Most of these reported reactions could be characterized by 1) relatively simple chemical transformations (that is, oxidation and hydrogenation), 2) use of metal-oxide (or active carbon or polymer)-supported AuNPs as a catalyst, and 3) involvement of gases (for example, O₂, CO, H₂, etc.) as a reactant. Albeit the reported reactions are important themselves, there have been few reports on the catalytic activities of AuNPs for C–C bond-forming reactions,^[10] which are ubiquitous and one of the most widely utilized organic transformations in synthetic organic chemistry.^[11]

The catalytic activity of AuNPs has been attributed to the adsorption of reactants, such as O₂ and CO, onto AuNPs (and/or Au/metal oxide interfaces).^[1b,c] Of interest, the reaction of CO with O₂ has been known to take place on the surfaces of AuNPs with an apparent activation energy of almost 0 kJ mol⁻¹.^[12] The selective hydrogenation of the C=

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O versus the C=C group in α,β -unsaturated aldehydes has been thought to be caused by the preferential adsorption of the C=O groups onto AuNPs.^[7a] In addition, the activation of CO₂ (presumably by CO₂ adsorption onto AuNPs) has been utilized to form cyclic carbonates and disubstituted ureas.^[13] Based on these findings, we reasoned that AuNPs could be catalytically active for some C–C bond-forming reactions, in which the activation of carbonyl groups (or possibly any functional groups containing lone pairs) is required, and herein we report the catalytic activity of AuNPs for C–C bond-forming reactions. We chose the cyanosilylation of aldehydes (reaction of aldehydes with trimethylsilyl cyanide (TMSCN))^[14] as a model reaction for investigating the catalytic activity of AuNPs, because the reactants had carbonyl



Scheme 1. AuNP-catalyzed cyanosilylation of aldehydes.

and lone-pair-containing cyano groups (Scheme 1). In addition, cyanohydrin trimethylsilyl ethers are industrially valuable intermediates in the synthesis of cyanohydrins, β -amino alcohols, α -hydroxy acids, and other biologically active compounds.^[15] It was reported that no reaction occurred between aldehydes and TMSCN in the absence of a catalyst.^[16] In this work, we synthesized AuNPs of Au⁰ oxidation state^[17] and studied the cyanosilylation of various aldehydes at room temperature with AuNPs as catalyst. The reaction mechanism was investigated in detail to determine whether the AuNP-catalyzed cyanosilylation was heterogeneous and/or homogeneous.

Results and Discussion

Synthesis and characterization of AuNPs: Figure 1a and b show a typical transmission electron microscopy (TEM) image and the size distribution of the synthesized AuNPs, respectively. The average diameter of the AuNPs and its standard deviation were 3.9 nm and 0.97, respectively, which were obtained by counting at least 150 particles. The synthesized AuNPs were also analyzed by X-ray photoelectron spectroscopy (XPS). In the survey scan, peaks from gold were shown at about 56.9 (5p_{3/2}), 83.7 (4f_{7/2}), 87.4 (4f_{5/2}), 335.0 (4d_{5/2}), 352.9 (4d_{3/2}), and 546.8 eV (4p_{3/2}) (Figure 1c). Carbon 1s (285.0 eV) and oxygen 1s (531.9 eV) peaks were also observed. The weak signal of bromine arose from N-(C₈H₁₇)₄Br, which was used as a phase-transfer reagent in the synthesis of AuNPs. The silicon peaks were due to the preparation method for sampling (see Experimental Section).

The inset in Figure 1c represents the XPS signature of the Au 4f doublet (4f_{7/2} and 4f_{5/2}). The peak position, line shape, and peak-to-peak distance of the Au 4f doublet are the important criteria to determine the oxidation state of gold.

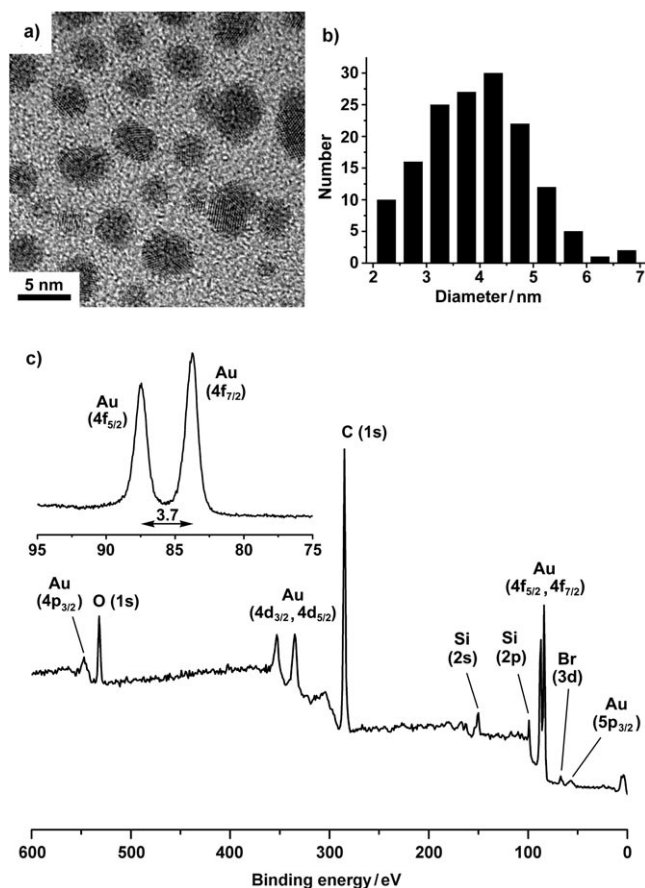


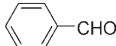
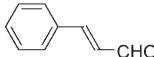
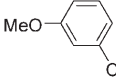

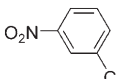
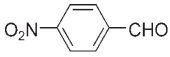


Figure 1. Characterization of synthesized AuNPs: a) TEM image, b) size distribution (average diameter: 3.9 nm), and c) X-ray photoelectron spectrum.

The binding energies for Au 4f_{7/2} and Au 4f_{5/2} were observed to be 83.7 and 87.4 eV, respectively; the peak-to-peak distance was 3.7 eV. These values are consistent with the Au⁰ oxidation state.^[17] If Au^I had been present, a peak (or at least a shoulder on the Au⁰ 4f_{5/2} peak) would have been expected near 84.9 eV. However, we did not observe any peak or shoulder from Au^I in the X-ray photoelectron spectrum. The absence of Cl signals indicates that the surface of the AuNPs was not contaminated by ionic species, such as Au^{III}Cl₄⁻ and Au^ICl₂⁻.^[10b, 18] In addition, AuNPs were not dissolved in polar solvents, such as water and methanol. Taken together, the characterizations confirmed that the synthesized AuNPs had the Au⁰ oxidation state.

Cyanosilylation of aldehydes: First, we investigated the catalytic activity of 1-octanethiol-protected AuNPs toward cyanosilylation of the α,β -unsaturated aldehyde, *trans*-cinnamaldehyde. The ¹H NMR spectrum showed almost 100% conversion of the aldehyde to the corresponding cyanohydrin trimethylsilyl ether after stirring for one hour. The peak at 9.57 ppm (–CHO) disappeared completely and a new peak at 5.11 ppm (–CHCNOTMS) was observed. The product was purified by column chromatography (hexane/ethyl acetate 10:1) in the form of the trimethylsilyl ether (yield of

isolated product 92%). In contrast, we could not observe any conversion at all in the absence of AuNPs, even after stirring for seven days at room temperature, which confirms that AuNPs were required for cyanosilylation. The resulting trimethylsilyl ethers of cyanohydrins were not stable during silica-gel chromatography except for *trans*-cinnamaldehyde, and thus the reaction yields were obtained by ^1H NMR spectroscopy with anisole as an internal standard. Table 1

Table 1. Cyanosilylation of aldehydes in the presence of AuNPs.

Entry	Substrate	t [h]	Yield [%] ^[a]
1		4	93
2		1	100 (92) ^[b]
3		12	100
4		4	98
5		48	94
6		72	22
7		3	97
8		4	100

[a] NMR spectroscopic yield. [b] Yield of isolated product.

shows the reactant scope of AuNP-catalyzed cyanosilylation.^[19] The reactions of aromatic aldehydes were almost quantitative (Table 1, entries 1–4), except for benzaldehyde derivatives containing an electron-withdrawing NO_2 group (Table 1, entries 5,6), and the reactions went smoothly in the case of aliphatic aldehydes (Table 1, entries 7,8). α,β -Unsaturated aldehydes seemed to be the most reactive: the conversion was quantitative in a short period of time (Table 1, entries 2,7).^[20]

We found that a gold thin film was also effective in catalyzing the cyanosilylation of aldehydes. The film was prepared by thermal evaporation of titanium (5 nm) and gold (100 nm) onto a silicon wafer (Si/SiO_2). The atomic force microscopy (AFM) image shows nanometer-sized features of gold: the hemispherical features had a lateral dimension of 50 nm on average (Figure 2). We immersed a freshly cleaned piece of gold ($\approx 1 \times 2$ cm) in a CDCl_3 solution containing *trans*-cinnamaldehyde (0.5 mmol), TMSCN (0.6 mmol), and anisole (0.5 mmol), and then the mixture was stirred at room temperature. The reaction went slower than with AuNPs: after 9 and 24 hours the conversion was 47 and 78%, respectively. However, when we increased the reaction temperature to 40°C, the reaction was complete in four hours. While we had difficulty in recycling AuNPs due to the unavoidable loss of AuNPs at each recycling step, the gold thin film made it easy to perform the recycling: we successfully recycled the gold thin film at least five times.

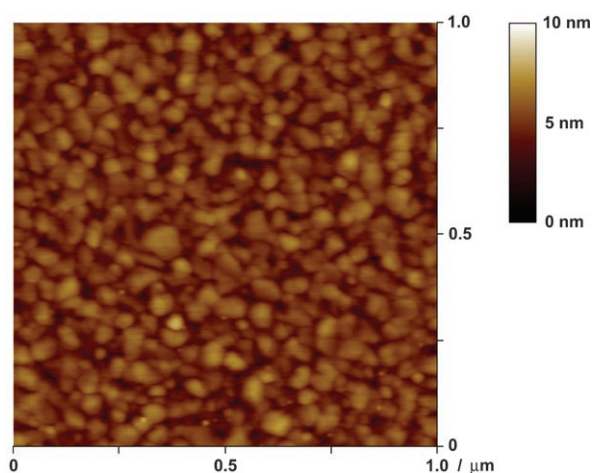


Figure 2. AFM image of bare gold thin films.

Interactions between reactants (aldehydes and TMSCN) and AuNPs:

Recent studies suggest that both CO and O_2 are adsorbed onto the surface of AuNPs to near saturation in the AuNP-catalyzed CO oxidation and that the rate-determining step is the reaction between the two adsorbed reactants (CO and O_2).^[21] For the AuNP-catalyzed $\text{C}=\text{O}$ hydrogenation of acrolein, the edges of AuNPs were identified as active sites for favoring the adsorption of $\text{C}=\text{O}$ groups of acrolein and subsequent reaction to allyl alcohol.^[7a] In addition, the cyclization of epoxides and the carbonylation of amines have been known to occur through the adsorption-driven activation of CO_2 .^[13] Based on these reports, we thought that aldehydes could be activated by adsorption onto AuNPs in the cyanosilylation of aldehydes and TMSCN.

NMR spectroscopy was used to verify the interactions between TMSCN and AuNPs. The addition of TMSCN to a CDCl_3 solution of AuNPs shifted a peak of the TMS group ($-\text{Si}(\text{CH}_3)_3$) from -1.82 to 1.91 ppm in the ^{13}C NMR spectrum and another peak of the TMS group ($-\text{Si}(\text{CH}_3)_3$) from -10.7 to 7.8 ppm in the ^{29}Si NMR spectrum.^[22] The observed downfield shifts in the NMR spectra indicate that TMSCN was adsorbed onto AuNPs.^[16]

Organocyanides have been reported to be adsorbed onto Au and other noble metals.^[23] From studies of metal cyanide complexes and the cyanide adsorbed onto metal surfaces by using electron energy-loss spectroscopy (EELS), XPS, and other techniques,^[24] it has generally been accepted that the linear coordination (σ bonding) through the lone-pair electrons of the nitrogen atom results in an increase of the $\text{C}\equiv\text{N}$ stretching frequency compared with that of the free organocyanide molecule. On the other hand, the coordination through the $\text{C}\equiv\text{N}$ π system has been known to result in a decrease of the $\text{C}\equiv\text{N}$ stretching frequency. We investigated the adsorption of TMSCN onto gold thin films by using IR spectroscopy (Figure 3). For free TMSCN molecules, the $\text{C}\equiv\text{N}$ stretching was observed at 2191 cm^{-1} , which was consistent with the reported value.^[25] When a gold thin film immersed in the TMSCN solution (CDCl_3 phase) was taken out,

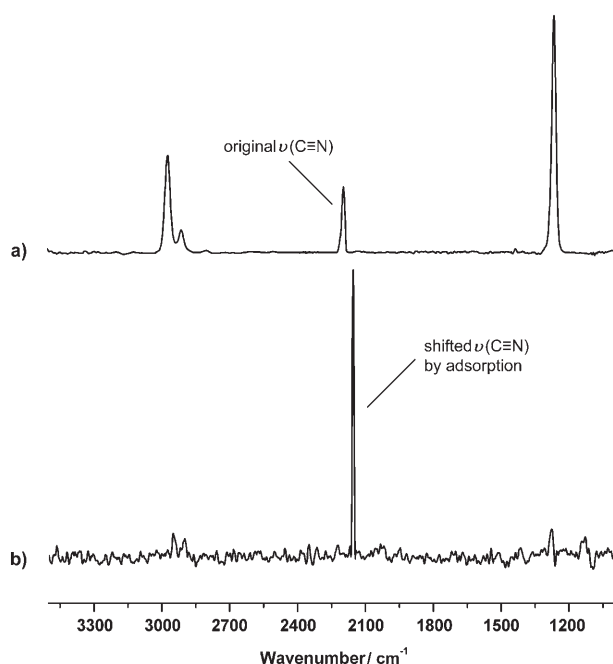


Figure 3. IR spectra of the gold thin film a) before and b) after the adsorption of TMSCN.

rinsed with chloroform, and analyzed by IR spectroscopy, the peak of the C≡N stretching appeared at 2156 cm^{-1} . The C≡N stretching band was red-shifted by 35 cm^{-1} . The red shift indicated that the adsorption of TMSCN onto the gold thin film, composed of hemispherelike gold nanostructures, occurred through the C≡N π system. In other words, the red shift can be attributed to the combined effects of $\pi(\text{CN})$ -to-metal electron donation and metal-to- $\pi^*(\text{CN})$ back-donation.^[23b] The red shift observed in the adsorption of TMSCN onto gold is opposite to the case of isocyanides. It was reported that the adsorption of organoisoocyanides onto gold led to an increase of the N≡C stretching frequency.^[9]

Dissolution of Au: The morphological change of AuNPs before and after the reaction was characterized by TEM. After the reaction, the TEM image showed the presence of an amorphous layer on the AuNPs (Figure 4a). This layer was thought to be the product that stuck on the surface of AuNPs, which is in agreement with a previous report.^[7a] Of interest, we also observed AuNPs the diameter of which was smaller than that of AuNPs before the reaction, indicative of the dissolution of gold during the reaction (Figure 4b). The dissolution of gold was also indirectly supported by inductively coupled plasma mass spectrometry (ICP-MS). We stirred a mixture of TMSCN and a gold thin film in CDCl_3 for 72 hours, and analyzed the solution phase by ICP-MS (we used a gold thin film instead of AuNPs, because it was practically difficult to separate the CDCl_3 phase from AuNPs completely). The ICP-MS data showed a small but detectable quantity of gold ($<1\text{ ppm}$) from the CDCl_3 phase. Therefore, the TEM and ICP-MS analyses suggest that TMSCN (and/or other species) dissolved gold from

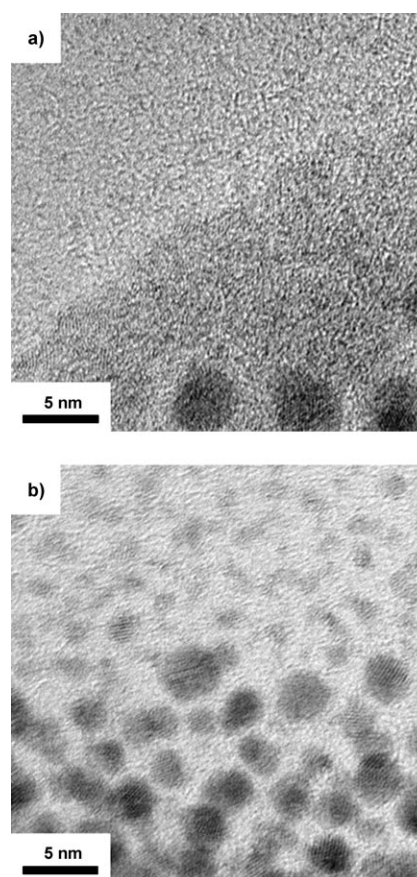


Figure 4. TEM images of AuNPs after the cyanosilylation.

AuNPs and newly generated species might catalyze the reaction. In particular, the TMSCN-induced dissolution of gold would generate AuCN or AuCN_2^- . Therefore, we investigated the catalytic activity of AuCN in the reaction. When we stirred a mixture of *trans*-cinnamaldehyde (0.5 mmol), TMSCN (0.6 mmol), and AuCN (1 mol %) in CDCl_3 for five hours at room temperature, we observed about 35% conversion. However, we did not observe any further increase in the conversion even after three days. As a comparison, *trans*-cinnamaldehyde was completely converted to trimethylsilyl ether in one hour with AuNPs as catalyst. In addition, KAuCN_2 did not catalyze the cyanosilylation of *trans*-cinnamaldehyde. Therefore, we thought that homogeneous catalysis participated in the reaction to some extent, but the exact species for the catalysis remains to be seen.

The TMSCN-induced dissolution of AuNPs would generate AuCN or its derivatives, but the observed catalytic efficiency of AuNPs could not be fully explained by only the catalytic activity of AuCN or its derivatives. Another possible species generated in the reaction mixture might be gold chloride species (AuCl_x), and this hypothesis was scrutinized experimentally. Recently, several researchers have reported that AuCl_x can be used as catalysts for some reactions, such as phenol synthesis,^[26a,b] ring expansion of cycloalcohols,^[26c] and the formation of heterobicyclic alkenes.^[26d] We examined whether AuNPs were dissolved by CDCl_3 and whether

or not dissolution might generate AuCl_x . It was practically difficult to entirely exclude the dispersed AuNPs from the CDCl_3 solution, and therefore the gold thin film was used instead of AuNPs. The film was immersed in CDCl_3 for 72 hours and then it was removed from the solution. We did not detect any gold species from the solution phase in the ICP-MS spectrum (<2 ppb), which indicates that CDCl_3 itself did not dissolve AuNPs.

Solvent effect: The catalytic activity of AuNPs toward the cyanosilylation of *trans*-cinnamaldehyde was also investigated with other solvents that did not contain chlorine. Table 2

Table 2. Cyanosilylation of *trans*-cinnamaldehyde with AuNPs in non-chlorinated solvents.

Solvent	<i>t</i> [h]	Yield [%] ^[a]
toluene	72	84
benzene	72	83
THF	3	90
DMF	72	7–8
DMSO	72	0

[a] NMR spectroscopic yield.

shows that AuNPs were catalytically active for the cyanosilylation in non-chlorinated solvents. AuNPs were most catalytically active in THF and inactive in relatively polar solvents, such as DMF and DMSO. We presume that the poor solubility/suspensibility of AuNPs in DMF and DMSO caused no (or little) catalytic activity in those solvents. The ICP-MS spectrum confirmed that no gold species existed in THF (<5 ppb). These results also indicate that AuCl (or its derivatives) was not involved in the reaction.

Mercury poisoning experiments: Based on all the results discussed above, we thought that the AuNP-catalyzed cyanosilylation proceeded by both heterogeneous and homogeneous mechanisms. Homogeneous catalysis would be achieved by leached gold species (presumably AuCN_x). The adsorption of the reactants (aldehydes and/or TMSCN) onto AuNPs of zero oxidation state would make heterogeneous catalysis proceed. Therefore, we needed to investigate the role of gold(0) in the reaction, and performed mercury poisoning experiments. Such experiments have been widely utilized as one of the most decisive tests for distinguishing homogeneous catalysis from heterogeneous catalysis, although careful precautions are required in the interpretation of experimental results.^[27] This test is based on the ability of the added mercury to poison metal(0) heterogeneous catalysts by either the formation of amalgam or adsorption onto the metal surface. Therefore, suppressed catalytic activity in the presence of mercury(0) is generally regarded as strong evidence for the presence of heterogeneous metal(0) catalysts.

We chose *m*-anisaldehyde as a model aldehyde, because the AuNP-catalyzed cyanosilylation proceeded slower than the reaction with *trans*-cinnamaldehyde. The conversion of *m*-anisaldehyde was complete in 12 hours, while that of

trans-cinnamaldehyde was complete in one hour. The slower conversion would make it easier to monitor the reaction. Figure 5 shows the results of mercury poisoning experi-

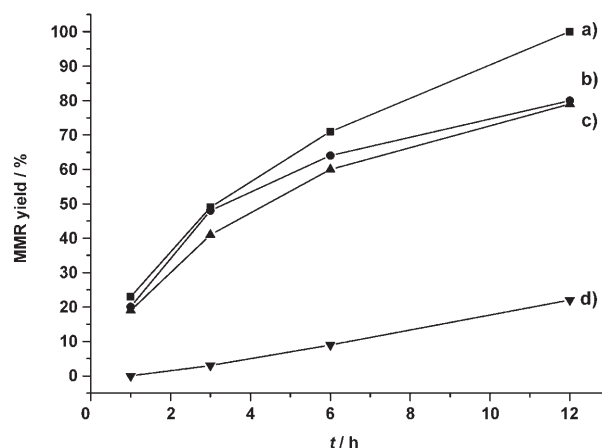


Figure 5. Mercury poisoning experiments with *m*-anisaldehyde. a) The reaction was performed without mercury. b) Mercury was added to the mixture after 1 h of reaction. c) Mercury was added at the beginning of the reaction. d) A mixture of mercury and AuNPs was stirred for three days and then the reactants were added.

Without mercury, the conversion increased continuously with time and reached 100% in 12 hours. When we added mercury to the mixture after reaction for one hour, we did not observe a complete suppression of the reaction, but observed a decreased conversion. The reaction became suppressed two hours after the addition of mercury and the conversion was 80% in 12 hours (Figure 5b). The mercury poisoning seemed to be slower than usual, therefore we added mercury to the reaction mixture at the beginning of the reaction. In this case, the suppression occurred a little earlier, but the final conversion after reaction for 12 hours is the same (80%; Figure 5c). Of interest, when we stirred a mixture of mercury and AuNPs in CDCl_3 for three days and added the reactants (*m*-anisaldehyde and TMSCN), we observed 20% conversion in 12 hours (Figure 5d).

The mercury poisoning experiments indicate that the AuNP-catalyzed cyanosilylation was catalyzed heterogeneously to some extent by nanometer-sized AuNPs of zero oxidation state and that mercury did not significantly affect the homogeneous catalysis by soluble gold species. A control experiment was also in accordance with the results. When we stirred a CDCl_3 solution of *trans*-cinnamaldehyde (0.5 mmol), TMSCN (0.6 mmol), and AuCN (1 mol%) for five hours at room temperature in the presence of mercury (1 mmol), the conversion was 35% and did not increase with longer reaction times. Without mercury, we obtained the same conversion after five hours.

Mercury would poison AuNPs by forming amalgam with them and the formation of amalgam was confirmed by X-ray energy-dispersive spectroscopy (EDS) by using scanning-mode TEM. A mixture of mercury and AuNPs was stirred in CDCl_3 for three days and then the resulting mix-

ture was analyzed. The TEM image showed black aggregates and amorphous shells (Figure 6); the amorphous shells existed around all black aggregates. EDS analysis along the

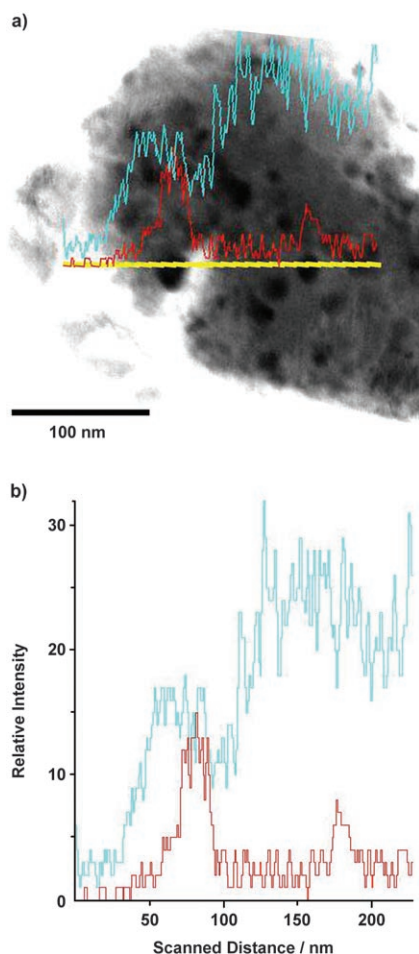
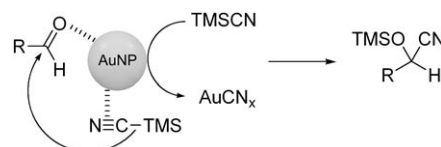


Figure 6. Line-scanning EDS analysis by using scanning-mode TEM after the mercury poisoning experiment. A mixture of mercury and AuNPs was stirred for three days. a) Line-scanning TEM image. The yellow line indicates the scanned area. b) The red and cyan lines represent the relative amounts of gold and mercury, respectively.

yellow line definitely revealed that the amorphous shells were composed of mercury and the black aggregates were composed of gold. The existence of mercury is represented as a cyan line and that of gold as a red line. Along the yellow line, the constituent ratio between mercury and gold was 10:1. In comparison, the EDS analysis of the synthesized AuNPs showed only gold peaks. Two possible explanations can be derived from the mercury poisoning and EDS results. One scenario is that the formation of amalgam would diminish the dissolution rate of gold and decrease the conversion yield. In this case, the observed catalytic effect of AuNPs would be derived solely from the leached gold species. However, the 35% conversion with only AuCN, as well as the observed decrease of the conversion upon addition of mercury, would support the explanation that mercury

suppressed the heterogeneous catalysis of gold(0) and the reaction proceeded both heterogeneously and homogeneously.

Proposed reaction mechanism: We propose that the observed catalytic activity of AuNPs for cyanosilylation of aldehydes could be explained by dual catalysis (heterogeneous and homogeneous catalysis; Scheme 2). In the heterogene-



Scheme 2. Proposed mechanism for AuNP-catalyzed cyanosilylation of aldehydes.

ous catalysis, the reactants (aldehydes and TMS-CN) are preferentially adsorbed onto the surface of AuNPs, presumably due to the nanoscopic property of AuNPs, and the activation energy of the reaction would become lowered by the adsorption.^[28] We assume that the contribution of heterogeneous catalysis to the reaction would be 20%, based on the mercury poisoning experiments. Regarding the homogeneous catalysis, we suggest TMS-CN-induced dissolution of gold for the generation of catalytically active, soluble species, such as AuCN, AuCN₂⁻, and/or Au^{III} species. However, we cannot completely exclude the possibility that AuNPs solely acted as a reservoir of the catalytically active gold species.

Conclusion

We performed a mechanistic investigation of the AuNP-catalyzed cyanosilylation of aldehydes. The detailed experiments indicated that the reaction proceeded via a combined pathway of heterogeneous and homogeneous catalysis. Although we could not identify the soluble species that were catalytically active in the reaction, both AuNPs and gold thin films were highly efficient for the cyanosilylation of various aldehydes. We believe that the coordination of both aldehydes and TMS-CN onto gold would facilitate the heterogeneously catalyzed reaction by lowering the activation energy. In addition to the coordination, the dissolution of gold seemed to contribute significantly to the reaction through homogeneous catalysis in the system investigated.

The newly discovered catalytic activity of nanometer-sized gold structures for organic transformations has prompted us to expand the usability of gold as a catalyst. The reported results open the possibility of the use of Au⁰, in the form of either nanoparticles or thin films, for other C–C bond-forming reactions.

Experimental Section

Materials: Hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, ACS reagent), tetraoctylammonium bromide ($\text{N}(\text{C}_8\text{H}_{17})_4\text{Br}$, 98%), 1-octanethiol ($\text{C}_8\text{H}_{17}\text{SH}$, 98.5%), benzaldehyde (redistilled, 99.5+%), *trans*-cinnamaldehyde (99%), *m*-anisaldehyde (97%), 3-nitrobenzaldehyde (99%), 4-nitrobenzaldehyde (98%), crotonaldehyde (predominantly *trans*, 99+%), butyraldehyde (purified by distillation, $\geq 99.5\%$), anisole (anhydrous, 99.7%), gold cyanide (AuCN , 99.99%), potassium dicyanoaurate(I) (KAuCN_2 , 98%), and phosphotungstic acid (hydrate, 99.995%) were purchased from Aldrich and used as received. Sodium borohydride (NaBH_4 , 98%, Junsei), *p*-anisaldehyde (99+%, Acros), TMSCN (96%, TCI), mercury (99.9995%, A.C.S. reagent, Sigma-Aldrich), toluene (HPLC grade, 99.9%, Merck), and absolute ethanol (99.8+%, Merck) were used as received. CDCl_3 (99.8%), $[\text{D}_8]$ toluene (99.5%), $[\text{D}_6]$ benzene (99.5%), $[\text{D}_8]$ THF (99.5%), $[\text{D}_7]$ DMF (99.5%), and $[\text{D}_6]$ DMSO were purchased from Cambridge Isotope Laboratories. Ultrapure water ($18.3 \text{ M}\Omega \text{ cm}^{-1}$) from the Human Ultra Pure System (Human Corp., Korea) was used.

Synthesis of 1-octanethiol-passivated AuNPs: AuNPs were synthesized by following the two-phase method.^[17] A yellow solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.284 mmol) in deionized water (25 mL) was prepared. $\text{N}(\text{C}_8\text{H}_{17})_4\text{Br}$ (0.667 mmol) as phase-transfer reagent was independently dissolved in toluene (25 mL) and added with rapid stirring to the aqueous solution of the Au salt. An immediate two-layer separation resulted, with an orange/red organic phase on the top and an orange-tinted aqueous phase on the bottom. The mixture was vigorously stirred until all color was removed from the aqueous phase, indicating quantitative transfer of the AuCl_4^- moiety into the toluene phase. Next, 1-octanethiol ($\text{C}_8\text{H}_{17}\text{SH}$; 0.5 mmol) was added to the rapidly stirred two-phase mixture at an Au/1-octanethiol molar ratio of 1:1.76. Upon the addition of 1-octanethiol, the aqueous layer immediately became beige/murky white. Finally, NaBH_4 (0.165 mmol) in deionized water (25 mL) was added to the rapidly stirred mixture. The color of the organic phase changed from orange to black/brown and then quickly to dark purple. The white precipitate and cloudiness in the aqueous phase dissipated as the reaction proceeded. The reaction was allowed to continue for 12 h with rapid stirring. After 12 h, the organic phase was separated and reduced in volume to 5 mL by rotary evaporation. The AuNPs were precipitated from the toluene solution by adding ethanol (300 mL) and cooling at -20°C for 12 h. The dark purple, 1-octanethiol-passivated AuNPs were then removed by centrifugation, washed five times with ethanol to remove excess 1-octanethiol, and dried under reduced pressure. 1-Octanethiol-passivated AuNPs were used for all the reactions employing AuNPs in this study.

Typical procedure for cyanosilylation of aldehydes: A CDCl_3 solution of aldehyde (0.5 mmol), TMSCN (0.6 mmol), and anisole (0.5 mmol) was prepared in a round-bottomed flask. AuNPs (0.2 wt % with respect to aldehyde) were added to the solution, and the resulting mixture was stirred at room temperature. The progress of the reaction was monitored by thin-layer chromatography (TLC) and the NMR yield (conversion %) was calculated by using anisole as an internal standard.

Mercury poisoning experiments: A CDCl_3 solution of *m*-anisaldehyde (0.5 mmol), TMSCN (0.6 mmol), and anisole (0.5 mmol) was prepared in a round-bottomed flask. AuNPs (0.2 wt %) were added, followed by mercury (1.0 mmol) after a predetermined time, and the resulting mixture was stirred at room temperature. The conversion of the reaction was calculated by ^1H NMR spectroscopy by using anisole as an internal standard.

Instrumentation: The synthesized AuNPs were characterized by TEM and XPS. For the TEM analysis, AuNPs dispersed in chloroform were dropped by using a micropipette onto a carbon-coated copper grid and the solvent was evaporated. All the TEM images were obtained with JEM-2010 and JEM-2100F instruments (JEOL, Japan). To obtain the TEM images of AuNPs after cyanosilylation of aldehydes, AuNPs were stained with phosphotungstic acid. For the XPS study, AuNPs dispersed in chloroform were dropped by using a micropipette onto a small piece of silicon wafer and the solvent was evaporated. X-ray photoelectron spectra were obtained with a VG-Scientific ESCALAB 250 spectrometer

(UK) with a monochromatized $\text{Al}_{\text{K}\alpha}$ X-ray source (1486.6 eV). Emitted photoelectrons were detected by a multichannel detector at a take-off angle of 90° relative to the surface. During the measurements, the base pressure was 10^{-9} – 10^{-10} Torr. Survey spectra were obtained at a resolution of 1 eV from one scan and high-resolution spectra were acquired at a resolution of 0.05 eV from three scans.

^1H NMR and ^{13}C NMR spectra were obtained with Bruker AVANCE 300 and AVANCE 400 spectrometers. ^{29}Si NMR spectra were obtained with Bruker AM-300 spectrometer. Chemical shifts in the ^1H NMR spectra were reported in ppm by using tetramethylsilane as an internal standard and CDCl_3 as a solvent. ^{13}C NMR spectra were reported in ppm relative to the center line of a triplet at 77.0 ppm of CDCl_3 . The IR spectrum of TMSCN was obtained from a thin film prepared by evaporation of CHCl_3 solution on a KRS-5 disk. The IR spectrum of gold thin films was obtained in single-reflection mode by using a dry N_2 -purged Thermo Nicolet Nexus FT-IR spectrophotometer equipped with the smart apertured grazing angle (SAGA) accessory. The *p*-polarized light was incident at 80° relative to the normal surface of the gold thin film, and a narrow-band mercury cadmium telluride (MCT) detector cooled with liquid nitrogen was used to detect the reflected light. We averaged 1000 scans to yield the spectrum at a resolution of 4 cm^{-1} . All IR spectra were reported in the absorption mode. The amount of leached gold was measured by ICP-MS (PQ3, VG Elemental).

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- 1) a) M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* **1987**, 405–408; b) M. S. Chen, D. W. Goodman, *Science* **2004**, *306*, 252–255; c) N. Valden, X. Lai, D. W. Goodman, *Science* **1998**, *281*, 1647–1650; d) M. M. Maye, Y. Lou, C.-J. Zhong, *Langmuir* **2000**, *16*, 7520–7523.
- 2) D. Astruc, F. Lu, J. R. Aranzas, *Angew. Chem.* **2005**, *117*, 8062–8083; *Angew. Chem. Int. Ed.* **2005**, *44*, 7852–7872.
- 3) a) D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science* **2006**, *311*, 362–365; b) H. Tsunoyama, H. Sakurai, Y. Negishi, T. Tsukuda, *J. Am. Chem. Soc.* **2005**, *127*, 9374–9375; c) N. Lopez, J. K. Nørskov, *J. Am. Chem. Soc.* **2002**, *124*, 11262–11263; d) R. J. H. Grisel, P. J. Kooyaman, B. E. Nieuwenhuys, *J. Catal.* **2000**, *191*, 430–437; e) S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G. J. Hutchings, *Chem. Commun.* **2002**, 696–697; f) C. Bianchi, F. Porta, L. Prati, M. Rossi, *Top. Catal.* **2000**, *13*, 231–236.
- 4) a) M. P. Kapoor, A. K. Sinha, S. Seelan, S. Inagaki, S. Tsubota, H. Hoshida, M. Haruta, *Chem. Commun.* **2002**, 2902–2903; b) T. Hayaishi, K. Tanaka, M. Haruta, *J. Catal.* **1998**, *178*, 566–575.
- 5) T. M. Salama, R. Ohnishi, M. Ichikawa, *Chem. Commun.* **1997**, 105–106.
- 6) M. D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings, F. King, E. H. Stitt, P. Johnston, K. Griffin, C. J. Kiely, *Nature* **2005**, *437*, 1132–1135.
- 7) a) C. Mohr, H. Hofmeister, J. Radnik, P. Claus, *J. Am. Chem. Soc.* **2003**, *125*, 1905–1911; b) P. Claus, A. Brückner, C. Mohr, H. Hofmeister, *J. Am. Chem. Soc.* **2000**, *122*, 11430–11439; c) J. Jia, K. Haraki, J. N. Kondo, K. Domen, K. Tamaru, *J. Phys. Chem. B* **2000**, *104*, 11153–11156.
- 8) a) H. Sakurai, A. Ueda, T. Kobayashi, M. Haruta, *Chem. Commun.* **1997**, 271–272; b) T. Tabakova, V. Idakiev, D. Andreeva, I. Mitov, *Appl. Catal. A* **2000**, *202*, 91–97.

- [9] M. Lazar, R. J. Angelici, *J. Am. Chem. Soc.* **2006**, *128*, 10613–10620.
- [10] a) S. Carrettin, J. Guzman, A. Corma, *Angew. Chem.* **2005**, *117*, 2282–2285; *Angew. Chem. Int. Ed.* **2005**, *44*, 2242–2245; b) A. K. Gupta, C. Y. Rhim, C. H. Oh, R. S. Mane, S.-H. Han, *Green Chem.* **2006**, *8*, 25–28. In these cases, a cationic gold species, Au^{III}, was the active species; c) H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi, T. Tsukuda, *Langmuir* **2004**, *20*, 11293–11296.
- [11] a) B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.* **2001**, *101*, 2067–2096; b) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731–1770; c) C.-H. Jun, *Chem. Soc. Rev.* **2004**, *33*, 610–618.
- [12] M. Haruta, *CATTECH* **2002**, *6*, 102–115.
- [13] F. Shi, Q. Zhang, Y. Ma, Y. He, Y. Deng, *J. Am. Chem. Soc.* **2005**, *127*, 4182–4183.
- [14] a) D. E. Fuerst, E. N. Jacobsen, *J. Am. Chem. Soc.* **2005**, *127*, 8964–8965; b) D. H. Ryu, E. J. Corey, *J. Am. Chem. Soc.* **2004**, *126*, 8106–8107; c) J.-M. Brunel, I. P. Holmes, *Angew. Chem.* **2004**, *116*, 2810–2837; *Angew. Chem. Int. Ed.* **2004**, *43*, 2752–2778; d) H. Gröger, *Chem. Eur. J.* **2001**, *7*, 5246–5251; e) B. Karimi, L. Ma'Mani, *Org. Lett.* **2004**, *6*, 4813–4815; f) R. J. H. Gregory, *Chem. Rev.* **1999**, *99*, 3649–3682.
- [15] C. G. Kruse in *Chirality in Industry* (Eds.: A. N. Collins, G. N. Shel-drake, J. Crosby), Wiley, Chichester, **1992**, Chapter 14.
- [16] M. Bandini, P. G. Cozzi, A. Garelli, P. Melchiorre, A. Umani-Ronchi, *Eur. J. Org. Chem.* **2002**, 3243–3249.
- [17] a) M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, *J. Chem. Soc. Chem. Commun.* **1994**, 801–802; b) D. V. Leff, L. Brandt, J. R. Heath, *Langmuir* **1996**, *12*, 4723–4730.
- [18] A. Kumar, S. Mandal, P. R. Selvakannan, R. Pasricha, A. B. Mandale, M. Sastry, *Langmuir* **2003**, *19*, 6277–6282.
- [19] For NMR spectra of the reactions, see the Supporting Information.
- [20] AuNPs were not effective in catalyzing ketones and imines compared with aldehydes. We observed 61% conversion of 2-pentanone after 72 h stirring at room temperature, but in other cases of ketones and imines the conversion was less than 10%. The increased loading of AuNPs did not improve the conversion.
- [21] a) M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet, B. Delmon, *J. Catal.* **1993**, *144*, 175–192; b) Y. Iizuka, T. Tode, T. Takao, K.-i. Yatsu, T. Takeuchi, S. Tsubota, M. Haruta, *J. Catal.* **1999**, *187*, 50–58; c) M. Haruta, *Gold Bull.* **2004**, *37*, 27–36.
- [22] For NMR spectra of the AuNP-TMSCN complex, see the Supporting Information.
- [23] a) M. F. Mrozek, S. A. Wasileski, M. J. Weaver, *J. Am. Chem. Soc.* **2001**, *123*, 12817–12825; b) D. H. Son, S. J. Ahn, Y. J. Lee, K. Kim, *J. Phys. Chem.* **1994**, *98*, 8488–8493; c) S.-W. Joo, T. D. Chung, W. C. Jang, M.-s. Gong, N. Geum, K. Kim, *Langmuir* **2002**, *18*, 8813–8816; d) H. A. Chun, D. W. Boo, K. Kim, M. S. Kim, *J. Mol. Struct.* **1990**, *216*, 41–52; e) C.-r. Lee, S. J. Bae, M.-s. Gong, K. Kim, S.-W. Joo, *J. Raman Spectrosc.* **2002**, *33*, 429–433; f) E. Lee, S. S. Yi, M. S. Kim, K. Kim, *J. Mol. Struct.* **1993**, *298*, 47–54; g) D. E. Richardson, H. Taube, *J. Am. Chem. Soc.* **1983**, *105*, 40–51.
- [24] a) H. Ibach, D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations*, Academic, New York, **1982**; b) B. A. Sexton, N. R. Avery, *Surf. Sci.* **1983**, *129*, 21–36; c) C. M. Friend, J. Stein, E. L. Muettterties, *J. Am. Chem. Soc.* **1981**, *103*, 767–772; d) K. Bange, R. McIntyre, J. K. Sass, N. V. Richardson, *J. Electroanal. Chem.* **1984**, *178*, 351–355; e) K. Kishi, S. Ikeda, *Surf. Sci.* **1981**, *107*, 405–416.
- [25] J. A. Seckar, J. S. Thayer, *Inorg. Chem.* **1976**, *15*, 501–504.
- [26] a) A. S. K. Hashmi, T. M. Frost, J. W. Bats, *Org. Lett.* **2001**, *3*, 3769–3771; b) A. S. K. Hashmi, M. Rudolph, J. P. Weyrauch, M. Wölfle, W. Frey, J. W. Bats, *Angew. Chem.* **2005**, *117*, 2858–2861; *Angew. Chem. Int. Ed.* **2005**, *44*, 2798–2801; c) J. P. Markham, S. T. Staben, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 9708–9709; d) L. Zhang, S. A. Kozmin, *J. Am. Chem. Soc.* **2005**, *127*, 6962–6963.
- [27] a) Y. Na, S. Park, S. B. Han, H. Han, S. Ko, S. Chang, *J. Am. Chem. Soc.* **2003**, *126*, 250–258; b) B. P. S. Chauhan, J. S. Rathore, M. Chauhan, A. Krawicz, *J. Am. Chem. Soc.* **2003**, *125*, 2876–2877; c) Y. Lin, R. G. Finke, *Inorg. Chem.* **1994**, *33*, 4891–4910; d) D. R. Anton, R. H. Crabtree, *Organometallics* **1983**, *2*, 855–859.
- [28] For heterogeneous catalysis, there was a report showing that chemical reactions can occur at the core surface of metal nanoparticles passivated with thiols. The hydrogenation reactions of allyl alcohol and maleic acid can be catalyzed by alkylthiol-passivated platinum nanoparticles and charged-thiol-passivated platinum nanoparticles, respectively (S. E. Eklund, D. E. Cliffel, *Langmuir* **2004**, *20*, 6012–6018). In our reaction system, the adsorption of the reactants onto 1-octanethiol-passivated AuNPs may not be achieved with ease. However, when the self-assembled monolayers (SAMs) of alkylthiols are formed on gold, the alkylthiol-coated gold surfaces are not perfect and contain various defects, such as pinholes, loosely packed SAMs, and large uncovered sites (X.-M. Zhao, J. L. Wilbur, G. M. Whitesides, *Langmuir* **1996**, *12*, 3257–3264; D. Losic, J. G. Shapter, J. J. Gooding, *Electrochem. Commun.* **2002**, *4*, 953–958). Therefore, we believe that the reactants can be adsorbed onto AuNPs at these defect sites. In addition, the defect sites also would be a starting site for the dissolution of gold (A. C. Templeton, M. J. Hostetler, C. T. Kraft, R. W. Murray, *J. Am. Chem. Soc.* **1998**, *120*, 1906–1911; R. Paulini, B. L. Frankamp, V. M. Rotello, *Langmuir* **2002**, *18*, 2368–2373; F. P. Zamborini, R. M. Crooks, *Langmuir* **1997**, *13*, 122–126).

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