Ligand effects in catalysis by atomically precise gold nanoclusters

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Atomically precise gold nanoclusters are ideal model catalysts with well-defined compositions and tunable structures. Determination of the ligand effect on catalysis requires the use of gold nanoclusters with protecting ligands as the only variable. Two isostructural Au38 nanoclusters, [Au38(L)20(Ph3P)4]2+ (L = alkynyl or thiolate), have been synthesized by a direct reduction method, and they have an unprecedented face-centered cubic (fcc)-type Au34 kernel surrounded by 4 AuL2 staple motifs, 4 Ph3P, and 12 bridging L ligands. The Au34 kernel can be derived from the fusion of two fcc-type Au20 via sharing a Au6 face. Catalytic performance was studied with these two nanoclusters supported on TiO2 (1/TiO2 and 2/TiO2) as catalysts. The alkynyl-protected Au38 are very active (>97%) in the semihydrogenation of alkynes (including terminal and internal ones) to alkenes, whereas the thiolated Au38 showed a very low conversion (<2%). This fact suggests that the protecting ligands play an important role in H2 activation. This work presents a clear demonstration that catalytic performance of gold nanoclusters can be modulated by the controlled construction of ligand spheres.

RESULTS AND DISCUSSION

The synthesis of Au38 nanoclusters was carried out by the direct reduction of gold precursors with NaBH4 in CH2Cl2. For cluster 1, the gold precursors are PhC≡CAu and Ph3P–AuX (X = anion), and for cluster 2, the gold precursors are m-MBT–Au and Ph3PAuX. The clusters were characterized by electrospray ionization–time-of-flight (ESI-TOF) mass spectrometry (MS) in positive mode (Fig. 1). The spectra show clean signals at a mass/charge ratio (m/z) of 5277.5 and 5498.3 for 1 and 2, respectively, which correspond to the molecular ions [Au38(PhC≡C)20(Ph3P)4]2+ and [Au38(m-MBT)20(Ph3P)4]2+. The observed isotopic pattern of the dicluster clusters agrees with the simulation (Fig. 1, inset). Thermogravimetric analysis (TGA) reveals that both clusters are stable below 155°C (fig. S1). X-ray photoelectron spectroscopy (XPS) revealed that the two Au38 nanoclusters have different Au 4f binding energies (1, 84.4 eV for Au 4f7/2 and 88.1 eV for Au 4f5/2; 2, 84.2 eV for Au 4f7/2 and 87.9 eV for Au 4f5/2), indicating different Au charge states (fig. S2). Infrared (fig. S3) bands at 1033 and 1263 cm−1 of SO3CF3 indicate the existence of SO3CF3− in 1 (42).

The structure of 1 was determined by single-crystal x-ray diffraction. As shown in Fig. 2, the Au38 nanocluster has a D3h symmetry and consists of 38 Au atoms, 20 phenylethynyl ligands, and 4 Ph3P ligands. The Au36 cluster has an fcc-type Au34 kernel surrounded by 4 PhC≡C–Au–C≡CPh staple motifs (Fig. 3A) and 12 bridging PhC≡C ligands (Fig. 3B). The structure of this Au34 kernel can be derived from the fusion of two Au20 via sharing a Au6 face. Catalytic performance was studied with these two nanoclusters supported on TiO2 (1/TiO2 and 2/TiO2) as catalysts. The alkynyl-protected Au38 are very active (>97%) in the semihydrogenation of alkynes (including terminal and internal ones) to alkenes, whereas the thiolated Au38 showed a very low conversion (<2%). This fact suggests that the protecting ligands play an important role in H2 activation. This work presents a clear demonstration that catalytic performance of gold nanoclusters can be modulated by the controlled construction of ligand spheres.

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Fig. 1. Mass spectra of the Au38 nanoclusters. Inset: Measured (black trace) and simulated (red trace) isotopic patterns. (A) [Au38(PhC≡C)20(Ph3P)4]2+ in 1. (B) [Au38(m-MBT)20(Ph3P)4]2+ in 2.
of two fcc-type Au$_{20}$ via sharing a Au$_6$ {100} face (Fig. 3C, highlighted in green). As shown in Fig. 3D, the fcc-type rodlike Au$_{20}$ is composed of two interpenetrating Au$_{13}$ cuboctahedra (Fig. 4D), which was previously observed in Au$_{38}$(SR)$_{20}$ (18). The Au$_{34}$ kernel has well-defined crystal faces exposed, that is, 8 trapezoid-shaped {111} facets on the front and backside of the gold core (fig. S4A, pale blue shadow) and 12 square facets {100} (fig. S4A, pale green shadow). Because of the fcc symmetry, the Au$_{34}$ kernel exhibits layer-by-layer abc packing of {111} atomic planes (Fig. 3C). The structure of 2 is very similar to 1, with PhC≡C–Au–C≡CPH motifs replaced by RS–Au–SR staples and PhC≡C bridges replaced by SR ligands (Fig. 3E).

In the Au$_{34}$ kernel of 1, the Au–Au distances from the four centered Au atoms (fig. S4B, highlighted in pink) to the peripheral Au atoms can be classified into two groups: shorter distances ranging from 2.7325(12) to 2.9138(9) Å and longer ones ranging from 2.9493(11) to 3.3017(12) Å with an average distance of 2.925 Å. It is comparable to the average Au–Au distance of 2.926 Å in 2. The Au–Au distances of the peripheral Au atoms range from 2.6992(11) to 2.8340(2) Å and 2.9085(12) to 3.4160(12) Å, giving an average distance of 2.940 Å. A comparable average distance of 2.958 Å is found in 2. The average Au–Au distances of Au$_{34}$ kernel in 1 and 2 are 2.940 and 2.946 Å, respectively, which are slightly longer than the 2.88 Å bond length in bulk gold, indicating that the interaction between Au atoms in Au$_{34}$ is strong. The four Au atoms of staples are linked to the double Au$_{20}$ cores, with an average Au–Au distance of 3.147 Å for 1 and 3.217 Å for 2. As shown in Fig. 3 (A and E), the SR groups link Au atoms via σ bonds in 2, whereas the alkynyls display both σ and π bonds in ligating Au atoms of 1.

Ultraviolet-visible (UV-vis) spectra of 1 and 2 in CH$_2$Cl$_2$ are shown in Fig. 4. From 350 to 1000 nm, although their metal core structures are almost identical and they are isoelectronic superatomic systems, the absorption profiles are significantly different. This difference suggests that the electronic structure can be disturbed by the surrounding organic ligands, for example, the alkynyl with a larger conjugated system. The HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) gaps are also different, with 1.49 eV for 1 and 1.37 eV for 2, which are comparable to the value of 1.5 eV of the body-centered cubic–type Au$_{36}S_2$(S-Adm)$_{20}$, but are much larger than the gap (0.9 eV) of the bi-icosahedral Au$_{38}$(SCH$_2$CH$_2$Ph)$_{24}$ (15, 43).

Clusters 1 and 2 are quite stable, as confirmed by monitoring the UV-vis spectra. No decomposition was observed after their solution was stored under ambient conditions for more than 1 month (fig. S5). The transmission electron microscopy (TEM) images of 1 and 2 indicate that the particles are uniform in size of about 1.4 nm (Fig. 4, inset), and it
agrees with that determined by x-ray structural analysis. These data indicate that the clusters maintain their nanosized structures in the solution and that their structural integrity in the solution is also supported by 31P nuclear magnetic resonance (NMR) (fig. S6). Single peaks were found at $d = 48.87$ parts per million (ppm) for 1 and 38.54 ppm for 2, which suggests that the four phosphorus atoms are in equivalent chemical environments due to the $D_2$ molecular symmetry.

Because 1 and 2 are isostructural, differing only in the protecting ligands, they are ideal platforms for studying the ligand effects on catalytic behavior. We chose the semihydrogenation of alkynes into alkenes as a probe reaction (44). The supported catalyst was made by impregnation of oxide powders in a CH2Cl2 solution of the Au38 nanoclusters, followed by drying and annealing at 130°C for 1 hour in a vacuum oven. Note that the free (unsupported) Au38 nanoclusters are stable below 155°C, as indicated by TGA (fig. S1).

To further confirm the thermal stability of Au38 nanoclusters, we treated the unsupported Au38 nanoclusters (powder) at 130°C in a vacuum tube for 1 hour and measured their absorption spectra. As shown in Fig. 5 (A and B), the Au38 nanoclusters have identical profiles before and after the thermal treatment, which indicates that they remain intact after the thermal treatment. ESI-MS analysis (Fig. 5, C and D) also confirms that no decomposition happened during the thermal treatment of Au38 nanoclusters because clean single peaks were observed at $m/z$ values of 5277.5 and 5498.3, which correspond to molecular ion peaks of $[\text{Au}_{38}(\text{PhC}≡\text{C})_{20}(\text{Ph}_3\text{P})_4]^{2+}$ and $[\text{Au}_{38}(\text{m-MBT})_{20}(\text{Ph}_3\text{P})_4]^{2+}$, respectively. Furthermore, the TEM images (fig. S7, A to C) show that the cluster size did not change significantly after being loaded on the TiO2 support and subjected to the thermal treatment.

The Au38/TiO2 catalysts were used in the semihydrogenation of alkynes, and the reaction products were analyzed by $^1H$ NMR spectroscopy (fig. S8). As shown in Fig. 6, neat TiO2 almost yielded no conversion, but it is important for $H_2$ activation. We tested the support effect by replacing TiO2 with Al2O3 and found that 1/Al2O3 yielded a much lower conversion ($<10 \%$). Under the same conditions (Table 1), catalyst 1/TiO2 yielded a >97% conversion (entries 1 to 5) for the semihydrogenation of alkynes, including terminal and internal ones. The turnover number is up to 88,195 within 24 hours. These results are in sharp

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**Table 1. Semihydrogenation of terminal* and internal† alkynes on Au38/TiO2 catalyst.**

| Entry | Catalyst | $R_1$ | $R_2$ | Conversion (%)‡ | Selectivity (%)‡ |
|-------|----------|-------|-------|-----------------|-----------------|
| 1     | 1        | Ph    | H     | 100             | 100             |
| 2     | PhC$_2$H$_4$ | H   | 100   | 100             |
| 3     | Ph      | Ph    | 100   | 93              |
| 4     | Ph      | 4-Br-Ph | 97 | 94              |
| 5     | Ph      | CH$_3$ | 97   | 94              |
| 6     | 2        | Ph    | H     | 1.6             |
| 7     | PhC$_2$H$_4$ | H   | 1.4              |
| 8     | Ph      | Ph    | 1.7              |
| 9     | Ph      | 4-Br-Ph | <1 |                  |
| 10    | Ph      | CH$_3$ | <1               |

*Reaction conditions: 80 mg of Au38 [0.4 weight % (wt %)]/TiO2 catalyst, 0.2 mmol of alkynes, 0.4 mmol of pyridine, 1.0 ml of EtOH/H$_2$O (10:1, v/v), 80°C, $H_2$ (10 bar), 15 hours. †Reaction conditions: 80 mg of Au38 [0.4 wt %]/TiO2 catalyst, 0.2 mmol of alkynes, 0.4 mmol of pyridine, 1.0 ml of EtOH/ H$_2$O (10:1, v/v), 110°C, $H_2$ (20 bar), 20 hours. ‡The conversion and stereo-selectivity for Z-alkenes were determined by $^1H$ NMR.

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**Fig. 4.** Optical absorption spectra of Au38 in CH$_2$Cl$_2$ and their TEM images. (A) TEM image of 1. (B) TEM image of 2. Black and red lines represent 1 and 2, respectively.

**Fig. 5.** UV-vis spectra and ESI-MS of Au38 in CH$_2$Cl$_2$. (A and C) UV-vis spectra and ESI-MS of 1. (B and D) UV-vis spectra and ESI-MS of 2. Black and red lines represent before and after thermal treatments, respectively.

**Fig. 6.** Activities of TiO2 and 1/TiO2 for the semihydrogenation of alkynes. (A) The substrate is ethynylbenzene [$H_2$ (10 bar)]. (B) The substrate is diphenylacetylene [$H_2$ (20 bar)].
contrast to those reported by Li and Jin (45). In their work, the terminal alkynes can be catalyzed by “ligand-on” Au35 catalysts, but internal alkynes cannot be catalyzed. With ligand-on catalysts, there is no room for the approaching of internal alkynes, so the alkynes must be activated by 1 in a different activation pathway; that is, it is not necessary for alkynes to be adsorbed on the cluster catalysts. The key step will be the activation of H2. The small H2 can be adsorbed on the nanocluster and then dissociate with the promotion of the base (pyridine). The generated hydrides are transferred to alkynes for reduction (46).

Whereas 1/TiO2 is very active, 2/TiO2 showed very low conversions (Table 1, entries 6 to 10). This fact indicates that the activation of H2 is influenced by the different electronic structures of the Au38 nanoclusters. Because the only structural difference between 1 and 2 is the protecting ligands, the electronic structures are disturbed by the types of the ligands. This hypothesis is supported by two facts: (i) The 31P NMR chemical shifts of 1 and 2 are different (Fig. S6), and (ii) their UV-vis spectra are significantly different (Fig. 4). The triple bond character of the alkyne favors the electronic mixing into the cluster kernel, which gives a more suitable electronic structure for the activation of H2. Note that Ouyang and Jiang (47) found that it is difficult for direct H2 activation on thiolate-protected gold nanoclusters.

Because 1 and 2 have different accompanying anions (SO3CF3 versus SbF6), we also prepared [Au38(m-MBT)20(Ph3P)4(SO3CF3)] (3) to make sure that the counterions do not affect the activities. Cluster 3 was prepared by anion exchange of 2 with KSO3CF3. We observed very similar activities on 2/TiO2 and 3/TiO2, confirming that the anions have no effect on the activity difference between 1/TiO2 and 2/TiO2.

To further reveal the roles of the ligands in H2 activation, we tested the catalytic performance of the supported nanoclusters with ligands being partially removed. We pretreated 1/TiO2 and 2/TiO2 at different temperatures to obtain catalysts with different ligand coverages. We found that 1/TiO2 pretreated at 175° or 220°C, that is, ligands partially removed, showed 100% conversion in the semihydrogenation of Au38 w a so b s e r v e d, a s c o n f i r m e db y T E M ( f i g . S 9 ) . T h i s f a c t


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prepared in a similar procedure, with m-MBTAu replacing PhC


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To further reveal the roles of the ligands in H2 activation, we tested the catalytic performance of the supported nanoclusters with ligands being partially removed. We pretreated 1/TiO2 and 2/TiO2 at different temperatures to obtain catalysts with different ligand coverages. We found that 1/TiO2 pretreated at 175° or 220°C, that is, ligands partially removed, showed 100% conversion in the semihydrogenation of diphenylacetylene (table S1). More E isomers were obtained with 1/TiO2 pretreated at a higher temperature (220°C) because the cluster surface is more accessible for the trans-type approach of the substrate. However, when all the ligands were removed, the naked gold cluster was hardly active (1/TiO2 pretreated at 400°C). Note that no severe aggregation of Au38 was observed, as confirmed by TEM (fig. S9). This fact indicates that alkyne plays a key role in the activation of H2. As for 2/TiO2, the activity is very low under all tested conditions (table S1, entries 6 to 9).

Thus, this work presents a clear example that the catalytic performance of gold nanoclusters can be modulated by the controlled construction of ligand spheres. Although the detailed activation mechanism is uncertain at present, future theoretical studies should be able to map it out.

CONCLUSIONS

Two novel fcc-type gold nanoclusters, [Au38(L)20(Ph3P)4]2+ (L = alkynyl or thiolate), have been synthesized, and they are isostructural, with the only difference being the L ligands. The unprecedented fcc-type Au34 kernel in the Au38 nanoclusters consists of two face-sharing Au35 units. Because the only structural difference between 1 and 2 is the protecting ligands, it offers ideal models to study the ligand effects in catalysis. The electronic structures are disturbed by the types of the ligands, which account for the different catalytic performances in the semihydrogenation of alkynes into alkenes. This work presents the first example of atomic-level understanding of the ligand effect on the catalytic properties of gold nanoclusters. In addition to the previously studied support and size effects, this work will draw more attention from synthetic, catalytic, and theoretical chemists in terms of understanding of the ligand effect.

MATERIALS AND METHODS

Synthesis

The detailed information about the synthesis of Au38 nanoclusters is provided in the Supplementary Materials. Briefly, for 1, a freshly prepared solution of NaBH4 (0.76 mg in 1.0 ml of ethanol) was added dropwise to a CH2Cl2 suspension (4.0 ml) of 0.15 mmol of PhC≡CAu and 0.05 mmol of Ph3PAuX (X = anion) under vigorous stirring. The color changed from pale brown to brown-red and finally to dark brown. After the reaction continued for 24 hours in air in the dark, the mixture was dried using a rotavapor to yield a dark solid, which was washed with ether (2 × 5 ml), dissolved in CH2Cl2 (1.6 ml), and then centrifuged for 4 min at 10,000 rpm. The resulting solution was subjected to diffusion with ether to afford black crystals after 3 weeks. Cluster 2 was prepared in a similar procedure, with m-MBTAu replacing PhC≡CAu.

Preparation of Au38/oxide and evaluation of catalytic performance

Typically, 2 mg of the Au38 nanoclusters was dissolved in 10 ml of CH2Cl2, and 500 mg of oxide was added. After stirring for 16 hours at room temperature, the Au38/oxide catalysts were collected by centrifugation and dried in vacuum. The catalysts were then annealed at 130°C for 1 hour in a vacuum tube. For the terminal alkynes, the reaction conditions were as follows: 80 mg of Au38 (0.4 wt %)/TiO2 catalyst, 0.2 mmol of alkynes, 0.4 mmol of pyridine, 1.0 ml of EtOH/H2O (10:1, v/v), 80°C, H2 (10 bar), and 15 hours. For the internal alkynes, the reaction conditions were as follows: 80 mg of Au38 (0.4 wt %)/TiO2 catalyst, 0.2 mmol of alkynes, 0.4 mmol of pyridine, 1.0 ml of EtOH/H2O (10:1, v/v), 110°C, H2 (20 bar), and 20 hours. The conversion and selectivity were determined by 1H NMR. The detailed method and characterization are available in the Supplementary Materials.

X-ray crystallography

Crystal data for 1 (C234H166F6O10P4S2Au38) were as follows: a = 25.664(13) Å; b = 42.83(1) Å; c = 44.30(3) Å; V = 48706(3) Å3; Fdd2, Z = 8; T = 100 K; 74,545 reflections measured; 8763 unique (Rint = 0.1055); final R1 = 0.0901; wR2 = 0.2915 for 7267 observed reflections [I > 2σ(I)]. Intensity data of 1 were collected on an Agilent SuperNova Dual system (Cu Kα). CCDC 1553284.

Crystal data for 2 (C210H202O4F12P4S20B2Au38) were as follows: a = 25.3576(5) Å; b = 25.3576(5) Å; c = 83.603(5) Å; V = 53757(4) Å3; I41/acd, Z = 8; T = 100 K; 44,481 reflections measured; 9656 unique (Rint = 0.0882); final R1 = 0.0792; wR2 = 0.2256 for 7828 observed reflections [I > 2σ(I)]. Intensity data of 2 were collected on an Agilent SuperNova Dual system (Cu Kα). CCDC 1553285.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/10/e1701823/DC1
Physical measurements
Synthesis
Characterization

fig. S1. TGA of 1 and 2.
fig. S2. XPS spectra of Au 4f in 1 and 2.
fig. S3. Fourier transform infrared spectrum of 1.
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