Supporting Information

Hydride-Doped Gold Superatom $(Au_9H)^{2+}$: Synthesis, Structure and Transformation

Shinjiro Takano,† Haru Hirai,† Satoru Muramatsu,† and Tatsuya Tsukuda†,‡*

†Department of Chemistry, School of Science, The University of Tokyo, Hongo 7-3-1, Bunkyo-Ku, Tokyo 113-0033, Japan

‡Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto 615-8520, Japan

Experimental

Chemicals

$HAuCl_4 \cdot 4H_2O$ was purchased from Tanaka Precious Metals. Solvents, CD_2Cl_2, ethanol-d_6, triphenylphosphine, and sodium borohydride were purchased from Wako Pure Chemical Industry. Tetrahydrofuran (dehydrated and stabilizer free) was purchased from Kanto Chemicals. Sodium borodeuteride was purchased from Cambridge Isotope Laboratories. The water used was Milli-Q grade (>18 MΩ). All commercially available reagents were used as received. An $Au(PPh_3)(NO_3)$ complex[1] was synthesized from the $Au(PPh_3)Cl$ complex obtained from $HAuCl_4 \cdot 4H_2O$.[2] An $[Au_{11}(PPh_3)_8Cl_2]Cl$ cluster was synthesized from the $Au(PPh_3)Cl$ complex.[3]

General

^1H (400 MHz) and $^{31}P\{^1H\}$ (162 MHz) NMR charts were recorded on a JEOL JNM-ECS400 spectrometer. Unless otherwise noted, all NMR experiments were conducted at 298 K. Chemical shifts of the ^1H NMR charts were referenced to the residual proton signal of the solvent (CD_2Cl_2: δ 5.32). Chemical shifts of the $^{31}P\{^1H\}$ NMR charts were referenced to 85% H_3PO_4 (δ 0.00) as an external standard. Positive-mode ESI-MS spectra were recorded on a JEOL JMS-T100LC time-of-flight mass spectrometer. A sample solution was directly infused at a flow rate of 3.0 mL/h via a syringe pump. Unless otherwise specified, the measurement parameters used were as follows: spray voltage 2.5 kV; ring electrode: 45 V; orifice 1 voltage: 40 V; orifice 2 voltage: 0 V; desolvation temperature 120°C; cone temperature 80°C. The spectra were calibrated using $[Cs(CsI)_n]^+$ clusters as an external reference, generated from a 99% aqueous methanol solution of CsI (0.5 mg/mL)

under the same parameters. The isotope patterns were calculated by mMass software.[4] UV-visible spectra were measured using a JASCO V-670 spectrophotometer with a 1 cm quartz cuvette. Microanalysis was carried out by the Microanalytical Laboratory, School of Science, The University of Tokyo.

Synthesis

Unless otherwise noted, syntheses were conducted under ambient conditions.

$[Au_9(PPh_3)_8](NO_3)_3$ (1)

The synthesis of cluster **1** was performed according to the reported procedure with modifications.[5] A 200 mL round bottomed-flask equipped with a magnetic stir bar was charged with $Au(PPh_3)(NO_3)$ complex (1.04 g; 2.00 mmol). 200 mL of absolute EtOH was added to the flask. The flask was equipped with three-way cock and a balloon filled with H_2 gas was connected. The atmosphere was replaced with H_2 gas by the evacuation and backfilling of H_2 gas for three cycles. Then, stirring was initiated and a white suspension resulted. Stirring was continued under the balloon pressure of H_2 gas and consumption of the starting material was almost complete after 24 h. The solvent was removed by rotary evaporator and 10 mL of CH_2Cl_2 was added. The solution was filtered through a paper filter and the solvent was evaporated. 50 mL of THF was added to the flask and the flask was left to stand for several hours. The supernatant was removed by decantation and the greenish residue was washed with THF and *n*-pentane giving a crude **1** with moderate purity (350 mg). The THF supernatant used for washing was dried and the residue was treated as described above with half the volume of EtOH. The second treatment gave a crude **1** with lower purity (370 mg). The combined crude product was dissolved in a minimum amount of MeOH (~20 mg/mL) and diethyl ether was allowed to diffuse into the MeOH solution. After one week, black green prisms were formed and the crystals were collected by filtration. The crystals were washed with diethyl ether and *n*-pentane and dried *in vacuo*. Yield: 600 mg (67% based on Au). ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.20–7.12 (m, 9H), 6.73 (t, 6H); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) δ: 57.4 (s). Anal. Calcd. for $[Au_9(P_1C_{18}H_{15})_8](NO_3)_3$: C, 42.63; H, 2.98; N, 1.04. Found: C, 42.39; H, 3.07; N, 1.11. UV-vis (CH_2Cl_2) λ_{max} (nm) = 315, 351(sh), 380(sh), 443.

$[Au_{11}(PPh_3)_8Cl_2](Cl, NO_3)$

A 50 mL round-bottomed flask equipped with a magnetic stir bar was charged with **1**

(101.5 mg; 25 μmol). 25 mL of CH_2Cl_2 was added to the flask and initiation of stirring gave a reddish orange solution. To the stirring solution was added a freshly prepared 0.10 M EtOH solution of $NaBH_4$ (250 μL; 25 μmol) causing a color change to dark red. Then, $Au(PPh_3)Cl$ complex (26 mg; 52 μmol) was added as a solid in one portion. The reaction was monitored by TLC (CH_2Cl_2:MeOH = 10:1) and the mixture was quenched by the addition of one drop of H_2O after 4 h. The solution was evaporated to dryness and the residue was recrystallized twice from CH_2Cl_2/(*i*-Pr)$_2$O. Cluster **5** was obtained as orange platelets. Yield: 64 mg (58% based on **1** assuming as a salt of NO_3). ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.30 (t(br), 6H), 6.93 (t, 3H), 6.68 (t, 6H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ: 52.8 (s).

in situ monitoring of the reaction by NMR

A 750 μL of CD_2Cl_2 solution of **1** (1 mM) was transferred to a 5 mm ϕ NMR tube equipped with a rubber septum and the atmosphere was replaced by Ar gas by means of freeze-pump-thaw cycling repeated three times. First, ^{1}H, ^{31}P{^{1}H}, and ^{1}H{^{31}P} NMR measurements of this degassed solution were conducted. Then, to the solution was added a freshly prepared 0.10 M ethanol-d_6 solution of $NaBH_4$ (7.5 μL) via syringe and the tube was shaken vigorously for a short period of time. The solution was introduced to the spectrometer and ^{1}H, ^{31}P{^{1}H} and ^{1}H{^{31}P} NMR measurements were performed using the same parameters. All measurements were done within 15 min after the addition of $NaBH_4$ solution. For the ^{1}H{^{31}P} NMR measurements, a selective decoupling of the ^{31}P nucleolus was conducted at the central frequency of 53.5 ppm with an irradiation pulse attenuation of 40 dB. The decoupling window was less than ±5 ppm since the ^{1}H{^{31}P} measurement with the decoupling at 59.3 ppm did not erase the spin–spin coupling of the H^- peak. After the measurements, the tube was stored in the spectrometer at 288 K for the following measurements.

DFT calculation

Electronic and geometric structures of $[Au_9(PMe_3)_8]^{3+}$ and $[Au_9H(PMe_3)_8]^{2+}$ (**3**) were studied by DFT calculations using the B3LYP functional. Basis sets used were LanL2dz for Au and 6-31G(d) for P, C, and H atoms. Singlet spin states were assumed for both $[Au_9(PMe_3)_8]^{3+}$ and **3**. Structural optimizations were carried out followed by frequency calculations to confirm that the optimized structures had no imaginary frequencies,

indicating that they were located at the local/global minima of the potential energy surfaces. Net charges of individual atoms were evaluated by natural population analysis based on natural bond orbitals (NBOs). All calculations were conducted using the Gaussian 09 program.[6]

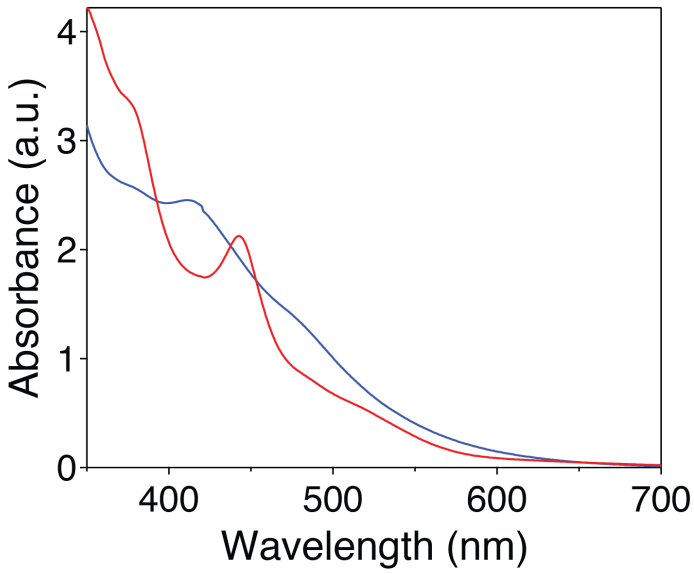

Figure S1. UV-vis spectra of **1**(red) in DCM and just after the addition of 0.1 M EtOH solution of $NaBH_4$ (1 eq.) to the solution of **1**(blue). The concentration of **1** was diluted one-tenth (0.1 mM) that of the original procedure (1 mM) as described in the main text.

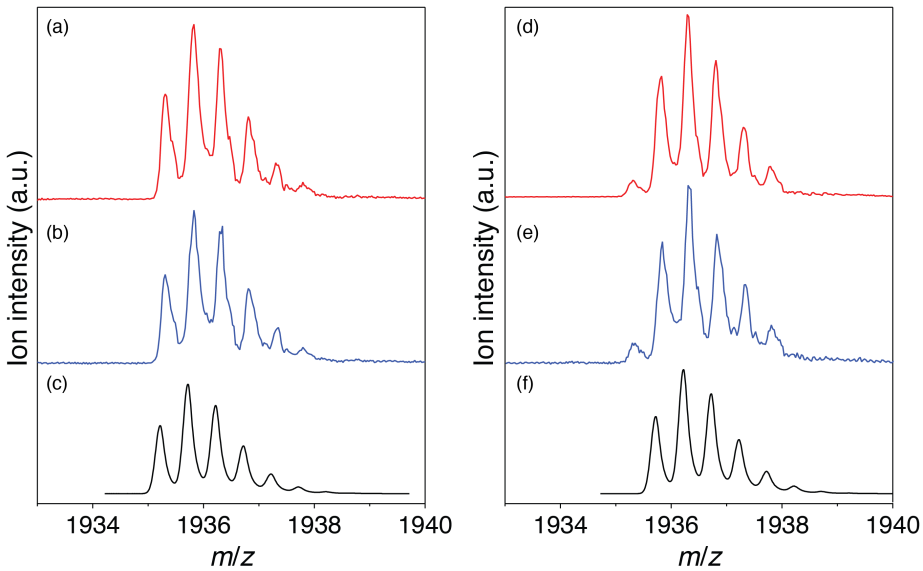

Figure S2. Positive-ion ESI-MS spectra of (a) just after, (b) 30 min after the addition of 0.10 M $NaBH_4$ (1 eq.) in ethanol-d_6 to **1** in DCM, (c) just after and (d) 30 min after the addition of 0.10 M $NaBD_4$ (1 eq.) in EtOH to **1** in DCM, respectively. Calculated isotope patterns of (c) $[Au_9H(PPh_3)_8]^{2+}$ and (d) $[Au_9D(PPh_3)_8]^{2+}$. The small monoisotopic peaks in (d) and (e) can be assigned to a residual $[Au_9H(PPh_3)_8]^{2+}$ cluster.

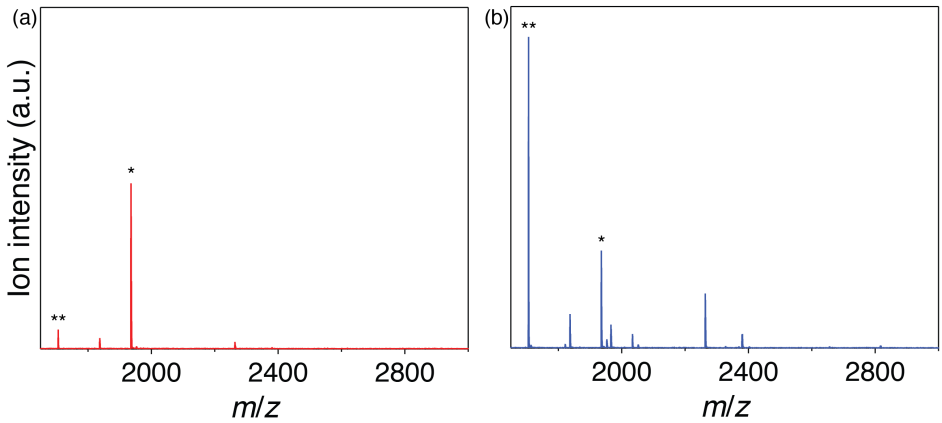

Figure S3. Positive-ion ESI-MS spectra of (a) just after and (b) 1 h after the addition of 0.10 M $NaBH_4$ (1 eq.) in EtOH to **1** in DCM. The spectra were recorded under the same conditions and are depicted at the same vertical scale. The asterisk (*) indicates the peak of $[Au_9H(PPh_3)_8]^{2+}$ and the double asterisk (**) indicates the peak of $[Au_8(PPh_3)_7]^{2+}$.

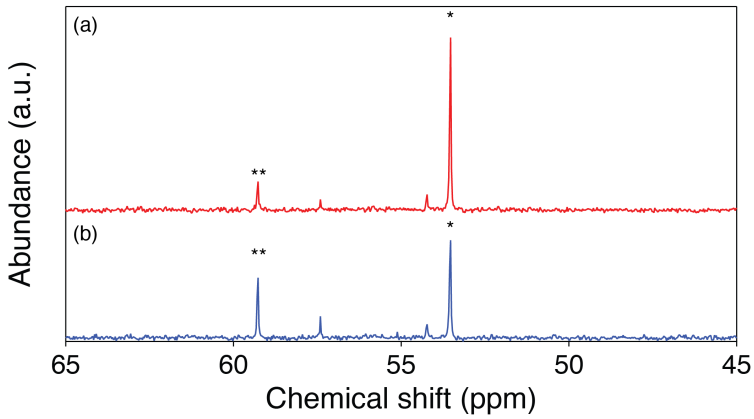

Figure S4. $^{31}P\{^1H\}$ NMR chart (a) just after and (b) 1h after the addition of 0.10 M $NaBH_4$ (1 eq.) in ethanol-d_6 to **1** in CD_2Cl_2 at 288 K. The asterisk (*) indicates the peak of $[Au_9H(PPh_3)_8]^{2+}$ and the double asterisk (**) indicates the peak of $[Au_8(PPh_3)_7]^{2+}$.

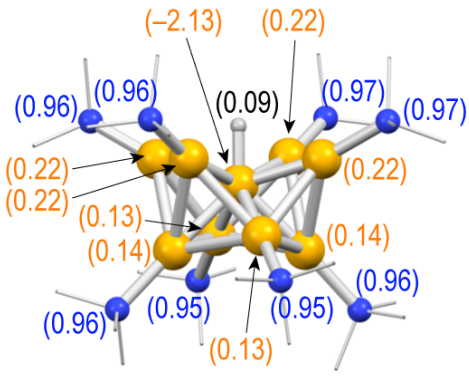

Figure S5. NBO charges of the individual atoms of $[Au_9H(PMe_3)_8]^{2+}$ (**3**).

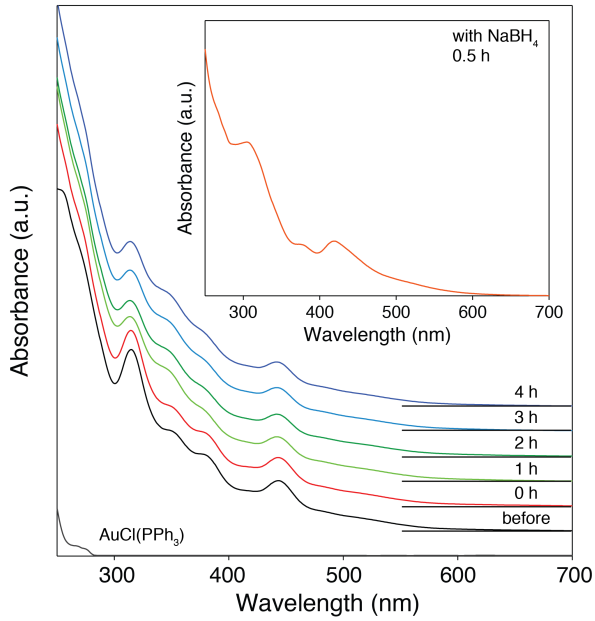

Figure S6. Temporal profiles of UV-vis spectra of **1** and 2.1 eq. of $AuCl(PPh_3)$ in DCM-EtOH (100:1) mixture in the absence of $NaBH_4$. For the UV-vis measurement, the mixture was diluted to one-fiftieth (0.02 mM) of the original solution (1 mM). Inset shows UV-vis spectrum of the mixture of **1**, 2.1 eq. of $AuCl(PPh_3)$ and 1 eq. of $NaBH_4$ recorded after 0.5 h.

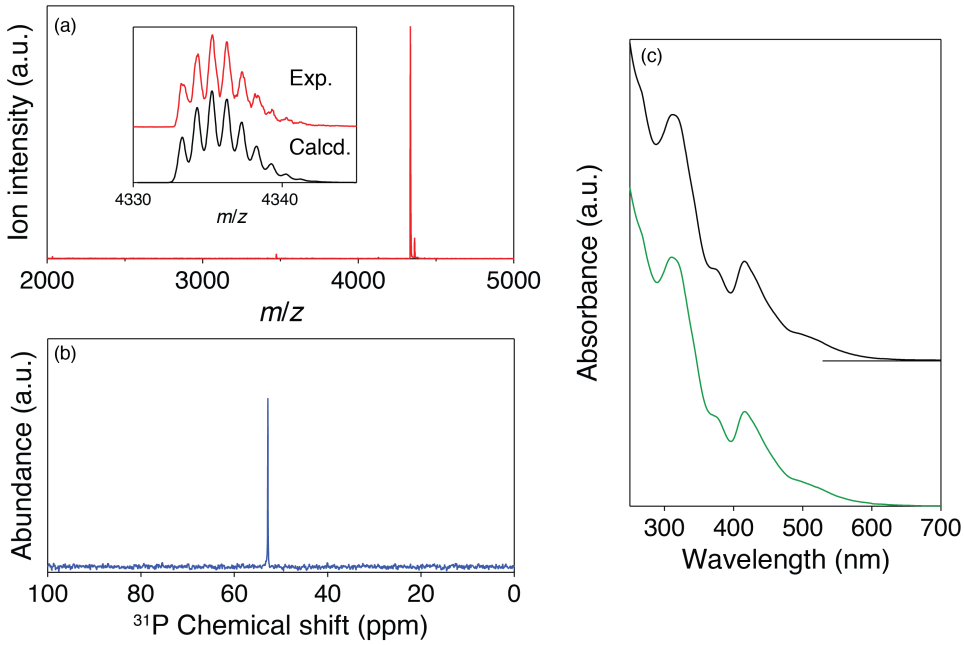

Figure S7. Spectral data for **5** obtained from **1** via H^- mediated growth. (a) Positive-ion ESI-MS spectrum. Inset shows the comparison between experimental and calculated isotope patterns. (b) $^{31}P\{^1H\}$ NMR chart of **5** in CD_2Cl_2. (c) UV-vis spectra of **5** (green) and $[Au_{11}(PPh_3)_8Cl_2]Cl$ (black) in DCM.

References

1. Mueting, A. M.; Alexander, B. D.; Boyle, P. D.; Casalnuovo, A. L.; Ito, L. N.; Johnson, B. J.; Pignolet, L. H. *Inorg. Synth.* **1992**, *29*, 280.
2. Gregory, B. J.; Ingold, C. K. *J. Chem. Soc. (B)* **1969**, 276.
3. McKenzie, L. C.; Zaikova, T. O.; Hutchson, J. E. *J. Am. Chem. Soc.* **2014**, *136*, 13426.
4. Strohalm, M.; Kavan, D.; Novák, P.; Volný, M.; Havlíček, V. *Anal. Chem.* **2010**, *82*, 4648.
5. Bos, W.; Bour, J. J.; Sterggerda, J. J.; Pignolet, L. H. *Inorg. Chem.* **1985**, *24*, 4298.
6. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.