

Article

## One-pot Synthesis of Au11(PPh2Py)7Br3 for the Highly Chemoselective Hydrogenation of Nitrobenzaldehyde

Chao Liu, Hadi Abroshan, Chunyang Yan, Gao Li, and Prof. Masatake Haruta

ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.5b02116 • Publication Date (Web): 18 Nov 2015

Downloaded from http://pubs.acs.org on November 23, 2015

## Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Catalysis is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

# One-Pot Synthesis of Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> for the Highly Chemoselective Hydrogenation of Nitrobenzaldehyde

Chao Liu<sup>†</sup>, Hadi Abroshan<sup>‡</sup>, Chunyang Yan<sup>†</sup>, Gao Li<sup>†,\*</sup>, and Masatake Haruta<sup>†</sup>

<sup>†</sup>Gold Catalysis Research Centre, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.

<sup>‡</sup>Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States.

**ABSTRACT:** In this study, gold clusters  $Au_{11}(PPh_3)_7Cl_3$  and  $Au_{11}(PPh_2Py)_7Br_3$  (PPh\_2Py = diphenyl-2-pyridylphosphine) are synthesized via one-pot procedure based on the wet chemical reduction method. The  $Au_{11}(PPh_3)_7Cl_3$  cluster is found to be active in chemoselective hydrogenation of nitrobenzaldehydes in the presence of hydrogen (H<sub>2</sub>) and a base (e.g., pyridine). Interestingly, the cluster with functional ligand PPh\_2Py shows similar activity without losing the catalytic efficiency in the absence of the base. The structure of the gold clusters and reaction pathway of the catalytic hydrogenation are investigated at the atomic/molecular level via UV-vis spectroscopy, electrospray ionization (ESI) mass spectrometry, and density functional theory (DFT) calculations. It is found that one ligand (PPh\_3 or PPh\_2Py) removal is the first step to expose the core of the gold clusters to reactants, providing an active site for the catalytic reaction. Then, the H–H bond of H<sub>2</sub> molecule becomes activated with the aid of either free amine (base) or ligand PPh\_2Py which is attached to the gold clusters. This work demonstrates promise of functional ligand PPh\_2Py in the catalytic hydrogenation to reduce the amount of materials (free base e.g., pyridine) that ultimately enter the waste stream, thereby providing a more environmentally friendly reaction media.

KEYWORDS: Au nanocluster, hydrogenation, chemoselective, DFT, amine

#### ■ INTRODUCTION

Gold clusters have become one of the most promising materials for applications in a wide range of nanoscience and nanotechnology owing to their quantum-size effects.<sup>1-4</sup> The gold clusters are stabilized by a wide range of organic ligands such as thiolate,<sup>5,6</sup> polymers,<sup>7</sup> carbenes,<sup>8</sup> amines,<sup>9</sup> alkynes,<sup>10,11</sup> and phosphines.<sup>12-13</sup> Atomically precise gold clusters (i.e., molecular purity, formulated as Au<sub>n</sub>L<sub>m</sub>, where L stands for ligand) have attracted considerable attention due to size-dependent properties that differ substantially from corresponding bulk materials.<sup>6</sup> The gold clusters have shown great potential in a wide range of applications such as optoelectronic nanodevices, biosensors, nanoelectronics, and novel catalysts.<sup>14-19</sup>

The gold clusters have been demonstrated to exhibit excellent catalytic performance in selective oxidation, hydrogenation, and carbon-carbon coupling reactions.<sup>17-21</sup> The stabilizing organic ligands play important roles in catalytic activity of the clusters.<sup>22-24</sup> For example, Leeuwen and coworkers reported on the application of the secondary phosphine oxide (SPO, (Naph)POH(<sup>t</sup>Bu), Naph = naphthyl)-protected gold cluster (core size: ca. 1.24 nm) in the chemoselective hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehyde to  $\alpha$ ,  $\beta$ -unsaturated alcohol using H<sub>2</sub> gas (40 bar) at 60 °C.<sup>24</sup> It is speculated that the SPO ligand plays a crucial role in the hydrogenation mechanism via the ligand–metal cooperative effects.

Pyridine was found to be an effective functional group for activation of reactants in the nanogold-catalyzed hydrogenation reactions.<sup>20,25</sup> According to a work by Yan *et al.*, gold nanoparticles catalyze the selective semihydrogenation of alkynes to alkenes using organosilanes with water as the hydrogen source.<sup>25</sup> They showed that an amine additive (e.g., pyridine) is required to suppress association of hydrogen atoms in

the hydrogenation reaction. In our very recent work, we presented that thiolate-protected  $Au_n(SR)_m$  clusters (-SR represents thiolate ligand, *n* and *m* varied from 15 to 99 and from 14 to 42, respectively) exhibit excellent catalytic activity in the chemoselective hydrogenation of aldehyde (e.g., nitrobenzaldehyde) to alcohols in the presence of pyridine.<sup>20</sup> Of note, catalytic active sites are located on the gold clusters and pyridine was found to act as the effective additive (promoter).

It is widely acknowledged that there should be significant changes in the operation of the chemical industry to reduce their negative impact on the environment. This tends towards what is commonly known as 'Green Chemistry' with principles formulated by the U.S. Environmental Protection Agency (US EPA) to design chemical products and processes that reduce or eliminate the generation of hazardous substances. Though pyridine is used as a solvent or additive in numerous chemical industries, it is toxic and not environmentallyfriendly even at low concentrations. Thus, it would be extremely worthwhile and desirable to synthesize new gold clusters with high catalytic performance in the absence of any amine additive (e.g., pyridine). In this study, we report on catalytic activity of gold clusters capped by functional ligands which contain pyridine group (e.g., PPh<sub>2</sub>Py). A key novel aspect of our present work is to bring pyridine groups close to surface gold to assist reactants' activation instead of using free base in reaction media. Such a novelty not only eliminates use of free base (e.g., pyridine) for the reactions but also markedly improves the probability of reactants' collision on the surface of catalysts, thereby increasing the reaction rate.

Herein, we present one-pot synthesis of an atomically precise gold cluster  $Au_{11}(PPh_2Py)_7Br_3$  and investigate its catalytic performance in the chemoselective hydrogenation of 4-

## EXPERIMENTAL METHODS

Synthesis of the Au clusters. In the case of Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub>, a freshly prepared solution of NaBH<sub>4</sub> (15.2 mg, 0.4 mmol) in ethanol (1 mL) was added dropwise to a stirred solution of [Au(PPh<sub>2</sub>Py)Cl] (40 mg, 0.13 mmol) and TOABr (85 mg, 0.15 mmol) in ethanol (10 mL). The solution color gradually turned to dark brown. After 12 h of stirring (at 600 rpm), the mixture was poured into water (10 mL). The dark solid was collected by centrifugation at 4,000 rpm and washed several times with hexane: $CH_2Cl_2$  (v/v = 5:1) to remove excess PPh<sub>2</sub>Py ligand and TOABr. The precipitated product was extracted by methanol (2 mL), followed by centrifugation again (at 10,000 rpm, 5 min) to remove insoluble components. The final products were obtained after drying the solution by rotary evaporation and stored in refrigerator. The production yield of Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> clusters based on consumption of Au(PPh<sub>2</sub>Py)Cl was found to be ca. 25%. It is worth mentioning that the yield of the same clusters in the absence of TOABr was ca. 15%. These results show that the use of a phase transfer catalyst like TOABr, which facilitates the migration of reactants between solution phases, leads to a higher production rate of Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> clusters.

The thiolate-protected  $Au_n(SPh)_m$  clusters are prepared by a reported literature method.<sup>20</sup> As shown in Figure S1 in the Supporting Information, the  $Au_{25}(SPh)_{18}$ ,  $Au_{36}(SPh)_{24}$ , and  $Au_{99}(SPh)_{42}$  clusters are well-characterized by UV-vis spectroscopy and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS).

Preparation of CeO<sub>2</sub>-supported gold cluster catalysts. Typically, 2 mg  $Au_n(SPh)_m$ ,  $Au_{11}(PPh_3)_7Cl_3$ or Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> clusters were dissolved in 10 mL dicholomethane, and then 200 mg CeO<sub>2</sub> powder was added. After stirring for 12 h at room temperature, the Au<sub>n</sub>(SPh)<sub>m</sub>/CeO<sub>2</sub>, Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub>/CeO<sub>2</sub>, and Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub>/CeO<sub>2</sub> catalysts were collected by centrifugation (at 1,000 rpm) and dried in vacuum. The catalysts were then annealed at 100  $^{\circ}$ C for ~ 1 h in a vacuum oven. Fourier-transform infrared (FT-IR) analysis was performed for the Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub>/CeO<sub>2</sub> catalyst before and after the 100 °C treatment in vacuum. The FT-IR spectra of the catalyst before and after the thermal treatment are superimposable (Figure S2 in the Supporting Information), strongly indicating that the Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> clusters on the surface of CeO<sub>2</sub> indeed remain intact. This is line with previous studies that the  $CeO_2$ -supported  $Au_n(SPh)_m$  clusters remain intact after the thermal treatment.<sup>11,20,21</sup>

**Characterization of gold nanoclusters.** The UV-Vis spectra of the clusters (dissolved in methanol) were acquired on a Hewlett-Packard (HP) Agilent 8453 diode array spectrophotometer at room temperature. Electrospray ionization (ESI) mass spectra were obtained using a Waters Q-TOF mass spectrometer equipped with a Z-spray source. The sample was dissolved in toluene (1 mg/ml) and then mixed with a dry methanol solution of CsOAc (50 mM) by a 1:1 vol ratio. FT-IR measurements were recorded on a Brukers/Tensor 27 instrument (resolution, 1 cm<sup>-1</sup>; scans, 8; range, 1000–4000 cm<sup>-1</sup>). MALDI-MS analysis was performed with a PerSeptive Biosystems Voyager DE super-STR time-of-flight (TOF) mass

spectrometer. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2propenyldidene]malononitrile was used as the matrix in MALDI-MS. Typically, 1 mg matrix and 0.1 mL analyte stock solution were mixed in 100  $\mu$ L CH<sub>2</sub>Cl<sub>2</sub>. 10  $\mu$ L of the solution was applied to the steel plate, and then air-dried prior to MALDI-MS experiment.

Typical procedure for chemselective hydrogenation reaction. In a typical selective hydrogenation reaction, 4nitrobenzaldehyde (0.05 mmol), pyridine (0.1 mmol), Au<sub>n</sub>(SPh)<sub>m</sub>/CeO<sub>2</sub> catalyst (100 mg, 1 wt% cluster loading) were added to an reactor (Parr instrument company, 22 mL capacity, series 4700) under 20 bar H<sub>2</sub>. Of note, in the case of the Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub>/CeO<sub>2</sub> catalyst, no pyridine was present. The reaction was carried out at 80 °C for 10 h as indicated in Table 1. After the catalytic reaction, the mixture was extracted by ethyl acetate. The crude product was obtained after the removal of the solvent. The conversion of 4-nitrobenzaldehyde and the selectivity for the 4-nitrobenzyl alcohol product were determined by <sup>1</sup>H NMR (300 MHz) spectroscopic analysis. In the recycling tests, the Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub>/CeO<sub>2</sub> catalyst was collected by centrifugation (at 1,000 rpm) for 5 min after the reaction and re-used in a fresh reaction.

**Computational details.** All calculations were performed using the Gaussian09 package with B3PW91 functional and LANL2DZ basis set (for Au) which have previously been shown to perform well to predict the structure of gold clusters.<sup>26-34</sup> For other elements the corresponding valence basis sets 6-31G\*\* together with the appropriate Stuttgart-Dresden effective core potentials (ECPs) were employed.<sup>35-38</sup> The energy change ( $\Delta E$ ) through a given reaction is determined by  $\Delta E$ =  $\Sigma E_{pro} - \Sigma E_{rea}$ , where  $\Sigma E_{pro}$  and  $\Sigma E_{rea}$  are total energy of isolated products and reactants in the reaction, respectively. The integral equation formalism polarizable continuum model (IEFPCM) was applied to study solvation effect on the stabilization of the clusters and complexes in water.<sup>39</sup>

#### RESULTS AND DISCUSSION

Synthesis and characterization of  $Au_{11}(PPh_2Py)_7Br_3$  cluster. The gold clusters were obtained by a facile one-phase process. In a typical synthesis,  $Au(I)(PPh_2Py)Cl$  and tetraoctylammonium bromide (TOABr) were dissolved in ethanol. The solution was stirred at room temperature. Next, sodium borohydride (NaBH<sub>4</sub>) dissolved in ethanol was added successively into the reaction mixture. The final products were obtained simply by centrifugation and purification.

Transmission electron microscopy (TEM) imaging of the as-obtained Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> cluster shows that the cluster's size is ca. 0.7–0.8 nm (Figure 1). Further, the gold cluster was analyzed by optical spectroscopy and electrospray ionization mass spectrometry (ESI-MS). The UV-vis spectrum of the Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> cluster shows a single-band at 406 nm and a shoulder between 450 and 550 nm (Figure 2A, red profile) similar to Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> cluster (Figure 2A, black profile).<sup>40,41</sup> Of note, peak at 406 nm for Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> is overall blue-shifted compared to that of Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> (412 nm). This is mainly due to electronic effect of the protecting organic ligand as it has also been observed in the case of Au<sub>25</sub>(SR)<sub>18</sub> (-SR = thiolate ligand).<sup>42</sup>

1

2

3 4

5

6 7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46 47 48

49

50

51

52

53

54

55

56

57

58

59

60



Figure 1. TEM image of as-obtained  $Au_{11}(PPh_2Py)_7Br_3$  cluster (core diameter  $\approx 0.7$ -0.8 nm). Scale bar: 10 nm.

To verify molecular formula of the as-obtained clusters, the monodisperse product-gold cluster is further characterized by ESI-MS and formulated indeed as Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> (Figure 2B). ESI-MS is considered as a "soft" ionization method and usually does not induce fragmentation of cluster during the analysis.<sup>43</sup> It is worth pointing out that no peaks are observed when no caesium acetate is present (Figure S3 in the Supporting Information). Therefore, cesium acetate (CsOAc, dissolved in methanol) was added to the solution to impart charges to the cluster. During the ESI-MS process, the Cs<sup>+</sup> ions attach to the cluster to form positively charged [cluster+ $Cs_x$ <sup>x+</sup> adducts. As shown in Figure 2B, there are three prominent peaks in range of 1500-6000 m/z (no peaks are found for m/z > 6,000); the observed peaks are centered at m/z= 4,381.87 (peak I), 2,257.43 (peak II), and 2,125.84 Da (peak III). In the zoom-in spectrum, the spacing of the experimental isotopic patterns of peak I is one, indicating that the ion carries +1 charge (Figure S4A in the Supporting Information). The spacing of the experimental isotopic patterns of peak II and III are 0.5, implying these ions are +2 charged (Figure S4B and S4C in the Supporting Information). The ESI-MS peaks are assigned as follows: peak I at m/z = 4381.87 Da to  $[Au_{11}(PPh_2Py)_7Br_3Cs_1]^+$  (theoretical *m/z*: 4382.13 Da, deviation: -0.26 Da), peak II at m/z = 2257.43 Da to  $[Au_{11}(PPh_2Py)_7Br_3Cs_2]^{2+}$  (theoretical *m/z*: 2257.55 Da, deviation: -0.12 Da), and peak III at m/z 2125.84 Da to  $[Au_{11}(PPh_2Py)_6Br_3Cs_2]^{2+}$  (theoretical *m/z*: 2125.88 Da, deviation: -0.04 Da). Of note, the experimental isotopic patterns of the peaks match quite well with simulated ones (Figure S4 in the Supporting Information).

The similarities in both the molecular formula ( $Au_{11}L_7X_3$ , L = PPh<sub>3</sub> or PPh<sub>2</sub>Py, X = Cl or Br) and UV-vis spectra indicate



**Figure 2.** (A) UV-vis spectra of the  $Au_{11}(PPh_2Py)_7Br_3$  and  $Au_{11}(PPh_3)_7Cl_3$  clusters. (B) Positive mode ESI mass spectrum of the  $Au_{11}(PPh_2Py)_7Br_3$  clusters in the presence of CsOAc.

that the structure of Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> cluster should be basically similar to that of Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub>. The skeleton of Au<sub>11</sub>clusters often has an approximate  $C_{3v}$  symmetry (incomplete centered icosahedron) that all the surface gold atoms are bound to either phosphine ligands or halogen atoms (Figure S5 in the Supporting Information).<sup>41</sup> In the case of Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> cluster, average atomic distance between surface Au atoms and C atom at the 2-position of the phenyl ring is ~3.62 Å (Figure S5 in the Supporting Information). Therefore, it is worthwhile to replace such C atom by N atom and examine if phosphine ligands with a functional group like 2-pyridine may promote the catalytic hydrogenation reaction without the aid of free base.

Catalytic performance of the Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> cluster in the chemoselective hydrogenation. The catalytic hydrogenation is carried out under the following conditions: 0.1 mmol 4nitrobenzaldehyde, 100 mg CeO<sub>2</sub>-supported gold cluster catalysts (1 wt% cluster loading), 1 mL water, 20 bar H<sub>2</sub> for 10 h (see details in the Experimental section). We chose CeO<sub>2</sub> oxide as support for the gold clusters. According to our previous work, CeO<sub>2</sub> leads to a better stability and higher catalytic efficiency of the supported clusters than other oxide-supports (e.g., TiO<sub>2</sub>, SiO<sub>2</sub>) in the catalytic hydrogenation reaction.<sup>20</sup>

**Table 1.** Comparison of the catalytic performance of the CeO<sub>2</sub>-supported gold clusters and complexes in the selective hydrogenation of 4-nitrobenzaldehyde to 4-nitrobenzyl alcohol.<sup>*a*</sup>

		$H_2$ NCs	HOH <sub>2</sub> C-	~>	NO <sub>2</sub>
	Au NCs	T (°C)	Base	Conv. $(\%)^b$	Select. $(\%)^b$
1	Au <sub>11</sub> (PPh <sub>3</sub> ) <sub>7</sub> Cl <sub>3</sub>	80	-	n.r.	-
2	$Au_{25}(SPh)_{18}$	80	-	n.r.	-
3	$Au_{36}(SPh)_{24}$	80	-	n.r.	-
4	$Au_{99}(SPh)_{42}$	80	-	n.r.	-
5	$Au_{11}(PPh_2Py)_7Br_3$	80	-	90	100
6	$Au_{11}(PPh_2Py)_7Br_3$	80	Ру	93	100
7	Au <sub>11</sub> (PPh <sub>3</sub> ) <sub>7</sub> Cl <sub>3</sub>	80	Ру	91	100
8	$Au_{25}(SPh)_{18}$	80	Ру	97	100
9	$Au_{36}(SPh)_{24}$	80	Ру	95	100
10	$Au_{99}(SPh)_{42}$	80	Ру	92	100
11	Au <sub>11</sub> (PPh <sub>2</sub> Py) <sub>7</sub> Br <sub>3</sub>	60	-	24	100
12	Au <sub>11</sub> (PPh <sub>3</sub> ) <sub>7</sub> Cl <sub>3</sub>	60	Ру	16	100
13	$Au_{25}(SPh)_{18}$	60	Py	15	100
14	$Au_{36}(SPh)_{24}$	60	Ру	14	100
15	$Au_{99}(SPh)_{42}$	60	Py	12	100
16	Au <sup>I</sup> (PPh <sub>2</sub> Py)Cl	80	-	81	$20 (80)^{c}$
17	Au <sup>I</sup> (PPh <sub>3</sub> )Cl	80	Ру	84	$24(76)^{c}$
$18^d$	Au <sub>11</sub> (PPh <sub>2</sub> Py) <sub>7</sub> Br <sub>3</sub>	80	-	87	100

<sup>*a*</sup>Reaction conditions: 100 mg CeO<sub>2</sub>-supported Au<sub>n</sub>L<sub>m</sub> cluster catalyst (ca. 1 wt% cluster loading), 1 mL water, 0.05 mmol 4-nitrobenzaldehyde, 0.1 mmol pyridine (Py), 20 bar H<sub>2</sub>, 10 h; <sup>*b*</sup>The conversion (Conv.) of 4-nitrobenzaldehyde and selectivity (Select.) for 4-nitrobenzyl alcohol were determined by NMR analysis. <sup>*c*</sup>The data given in the parentheses is selectivity for 4-aminobenzaldehyde. <sup>*d*</sup>Reaction conditions: 3 g Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub>/CeO<sub>2</sub> catalyst (~30 mg Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> loading) in 30 mL water, 5 mmol 4-nitrobenzaldehyde, 20 bar H<sub>2</sub> at 80 °C, 20 h. n.r. = no reaction.



Scheme 1. (A) Structure of  $Au_{11}(PPh_3)_7Cl_3$  cluster.<sup>41</sup> Detachment of a halide anion and a phosphine ligand results in (B)  $[Au_{11}(PPh_3)_7Cl_2]^+$  and (C)  $Au_{11}(PPh_3)_6Cl_3$  with an open metal site on the cluster. Color codes: Au, green; P, purple; Cl, cyan. All the carbon and hydrogen atoms are omitted for clarity.

First, we find that no conversion (nitrobenzaldehyde  $\rightarrow$  nitrobenzyl alcohol) is achieved by using Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub>/CeO<sub>2</sub> catalyst in the absence of the base (Table 1, entry 1). Catalytic activity of thiolate-protected gold clusters (e.g., Au<sub>25</sub>(SPh)<sub>18</sub>, Au<sub>36</sub>(SPh)<sub>24</sub>, and Au<sub>99</sub>(SPh)<sub>42</sub>) were also examined under the same reaction conditions. As shown in Table 1 (entries 2-4), no product formation was observed in these cases, as well. However, such catalysts yield a high conversion in the presence of two molar equivalent of pyridine at 80 °C (Table 1, entries 7-10), in consistent with our previous studies.<sup>21</sup> The most salient feature of Table 1 is the gold clusters with functional ligand PPh<sub>2</sub>Py exert a major influence on the conversion of nitrobenzaldehyde. When Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> is used, the conversion reaches to 90% even in the absence of free base like pyridine (Table 1, entry 5). The turnover frequency (TOF = [reacted mol of nitrobenzaldehyde]/[(mol of Au cluster) × (reaction time)]) of the reaction is found to be ca. 20 h<sup>-1</sup>. Several reasons can lead to a low TOF including; (1) slow diffusion/adsorption of the reactants towards the catalyst, and (2) low number of active site per catalyst. In our case, we think the later reason is important to consider as there is one active site per catalyst (see the proposed mechanism below). Of note, the catalytic activity of the Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> does not change when free pyridine was added into the reaction media (Table 1, entry 6). These results strongly indicate that the PPh<sub>2</sub>Py ligands are indeed promoter for the catalytic reaction using  $Au_{11}(PPh_2Py)_7Br_3$ . The lower temperatures reduce the reaction conversion (Table 1, 60 °C vs. 80 °C). However,  $Au_{11}(PPh_2Py)_7Br_3$  shows a better catalytic activity among all the gold clusters considered in this study at the lower temperature (60 °C). Notably, almost 100% chemoselectivity for the alcohol product was observed in all the catalytic reactions (Table 1). These experimental results indicate that the PPh<sub>2</sub>Py ligands on the gold clusters play a crucial role to promote the catalytic hydrogenation.

Further, the conventional gold nanoparticles (bared), supported on CeO<sub>2</sub> were tested in the hydrogenation of nitrobenzaldehydes under the identical reaction conditions (in the presence of pyridine and H<sub>2</sub>). A 100% selectivity towards nitrobenzyl alcohol product was obtained, which is similar to those achieved by Au<sub>11</sub> clusters. To make sure that the observed activity of Au<sub>11</sub> clusters is due to a heterogeneous catalysis and not a homogeneous one, we examined catalytic activity of two gold complexes: Au<sup>I</sup>(PPh<sub>2</sub>Py)Cl and Au<sup>I</sup>(PPh<sub>3</sub>)Cl. Results show that the homogeneous catalysts lead to hydrogenation of nitro group over aldehyde (Table 1, entries 16 and 17). These results are totally different compared to those obtained using Au<sub>11</sub> clusters (Table 1, entries 5-15) and ligand free gold nanoparticles, which confirm the heterogeneous nature of the catalysis by the gold clusters.

To test the performance of the catalyst in large scale synthesis, we examined the activity of the  $Au_{11}(PPh_2Pv)_7Br_3/CeO_2$  in a scaled up catalytic system under reaction conditions as indicated in Table 1, entry 18. The reaction conversion and selectivity for 4-nitrobenzyl alcohol product were found to be 87% and 100%, respectively (Table 1, entry 18). These results are close to those reported as entry 5 of Table 1 for the smaller scale (90% and 100%, respectively). Therefore, the  $Au_{11}(PPh_2Py)_7Br_3/CeO_2$  is characterized as a good catalyst for large scale catalysis.

we Next. investigated the recyclability of Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub>/CeO<sub>2</sub> catalyst. The Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub>/CeO<sub>2</sub> catalyst was collected by centrifugation (at 1,000 rpm for 5 min) after the reaction, washed with water and ethyl acetate, and dried in an oven. The catalyst thus prepared was then reused in a fresh reaction medium under the identical reaction conditions at 80 °C. The recycled catalyst showed the same activity and selectivity as the fresh catalyst (Figure S6). No appreciable loss of catalytic activity and selectivity was observed after 4 cycles (higher cycles were not tested). Thus, the Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub>/CeO<sub>2</sub> catalyst appears to be relatively robust and holds promise as a practically useful catalyst in the chemoselective hydrogenation process.

Structure and characterization of Au<sub>11</sub>(PPh<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> species. Extensive studies on bare gold clusters without ligands attached have revealed that low-coordinated naked gold atoms on the surface are the main active sites for catalytic reactions.<sup>19,44-46</sup> All the surface gold atoms of Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> and Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> clusters are bound to phosphine ligands (PPh<sub>3</sub> and PPh<sub>2</sub>Py) and halogen atoms (Cl or Br). This raises an important question as to the nature of the active sites for hydrogenation reactions catalyzed by the gold clusters. Therefore, we first speculated that the gold clusters may lose either a phosphine ligand or a halogen atom under reaction conditions to provide an open metal site for the catalytic reaction (Scheme 1). DFT calculations on framework of  $Au_{11}(PPh_3)_7Cl_3$ ,<sup>41</sup> revealed that the open metal site produced via removal of a halide anion (noted as Au1, Scheme 1B) is inert toward H<sub>2</sub> adsorption in the presence or absence of a base (e.g., NH<sub>3</sub>). However, removal of a phosphine ligand provides an open metal site (noted as Au2, Scheme 1C) which was found to adsorb H<sub>2</sub> in the presence of the base. Of note, there is no strong interaction between H<sub>2</sub> and Au2 in the absence of ammonia, in agreement with our experimental results (Table 1, entry 2). As a result, our DFT calculations propose that hydro-ACS Paragon Plus Environment

1

Page 5 of 8

 $Au_{11}(PPh_3)_6Cl_3$  species which should be generated from its parent cluster  $Au_{11}(PPh_3)_7Cl_3$ .



**Figure 3.** (A) Positive mode ESI mass spectra of  $Au_{11}(PPh_3)_7Cl_3$  cluster in the presence of ammonia (condition: 80 °C, 4h). (B) Thermal stability of  $Au_{11}(PPh_3)_7Cl_3$  cluster in a closed cuvette (dissolved in ethanol at 80 °C for 12h).

To test the notion driven from DFT calculations, we prepared an ethanol solution of the Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> cluster in the presence of ammonia string at 80 °C. The UV-vis spectrum of the Au cluster was monitored for 12 h (Figure 3B). We observed that the distinct peak at 412 nm gradually red-shifted by 9 nm, which indicates a slight structural change in the gold cluster. The ESI-MS results of the cluster are shown in Figure 3A. Only one peak at m/z = 1989.66 Da is observed in the range of 1500 to 4000 of ESI-MS profile (in positive mode). The spacing of the experimental isotopic pattern of the peak is 0.5 (Figure S7 in the Supporting Information) which indicates an ion with a net charge of +2. The molecular ion is assigned to  $[Au_{11}(PPh_3)_6Cl_3Cs]^{2+}$  (theoretical m/z: 1989.50 Da, deviation: +0.16 Da) with the experimental isotopic patterns matching well with simulated ones (Figure S7 in the Supporting Information). These results strongly imply that one phosphine ligand is removed from the gold cluster in the presence of a base (e.g., ammonia) at 80 °C, in good agreement with our DFT results. The ESI-MS results (Figure 2B, peak III) also

indicate the Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>6</sub>Br<sub>3</sub> species may also exist in the reaction media while Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>2</sub> is not observed. These results strongly indicate that one ligand (PPh<sub>3</sub> or PPh<sub>2</sub>Py) removal is the first step to expose the core of the gold clusters to reactants, thereby providing an active site for the catalytic reaction.

Hydrogenation mechanism catalyzed by Au<sub>11</sub> cluster. We next propose a mechanism for hydrogenation of benzaldehyde catalyzed by Au<sub>11</sub>(PPh<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> and Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>6</sub>Br<sub>3</sub> species which are generated from their parent clusters Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> and Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub>. DFT calculations are performed to rationalize the mechanism of hydrogenation reaction catalyzed by the Au<sub>11</sub> clusters promoted by amines (e.g., pyridine). The framework of the Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> cluster is adopted from its crystal structure for the calculations.<sup>41</sup> Our ESI-MS and UVvis results strongly suggest that  $Au_{11}(PPh_3)_7Cl_3$  and Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> clusters must basically have the same molecular structure. Therefore, mechanistic insights offered by DFT using Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> framework can be informative for the case of Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> cluster, as well. We later comment on the differences between Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> and Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> clusters. Specifically, the roles played by the functional ligand PPh<sub>2</sub>Py are discussed in details.

Upon removal of a phosphine ligand from Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> to form Au<sub>11</sub>(PPh<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> (**Re**, Figure 4), H-H bond of a H<sub>2</sub> molecule is activated on site Au2 (Scheme 1C) of the cluster with the help of a base like ammonia ( $\mathbf{Re} \rightarrow \mathbf{Im1}$ , Figure 4). Note, pyridine group is replaced by ammonia to reduce the computational demand. According to DFT calculations, the adsorption energy ( $\Delta E$ ) of H<sub>2</sub>—NH<sub>3</sub> is -8.0 kcal/mol in gas phase (Table 2). While the gas-phase results offer useful insight, it is worthwhile to account solvation effects for both qualitative and quantitative understanding of reactions pathways in solution. Specifically, in a polar environment like H<sub>2</sub>O, charged species become stabilized through electrostatic interactions with the solvent, compared to the neutral ones. The polarizable continuum model (PCM) calculations indicate that  $\Delta E$  of **Re**  $\rightarrow$  Im1 in water is -22.0 kcal/mol which shows the product state (Im1) becomes considerably stabilized compared to the reactants because of the highly charge-separated nature of the  $NH_4^+...H^-$  moiety. We note that upon adsorption of  $H_2$ — $NH_3$ , the H–H atomic distance is elongated to 0.82 Å, much longer than that for an isolated  $H_2$ —NH<sub>3</sub> in the gas phase (0.75 Å). This bond length is even extend to 1.83 Å in PCM calculations indicating that  $H_2$  bond is completely broken to form  $NH_4^+$ with H<sup>-</sup> on site Au2. The atomic distances are summarized in Figure 4.

According to the experimental results, we assume pyridine group of the phosphine ligands of  $Au_{11}(PPh_2Py)_6Br_3$  acts as a base like ammonia to activate the H<sub>2</sub> bond via its lone pair of electrons. The ammonium ion formed in previous step may become solvated in the reaction media and act as a donor for protonation of aldehyde (Im1  $\rightarrow$  Im2, Figure 4). This step was found to be endothermic by +10.7 kcal/mol in water, while it

Table 2. DFT results for energies (kcal/mol) for elementary steps of proposed mechanism in Figure 4.

$\operatorname{Au}_{11}(\operatorname{PPh}_3)_6\operatorname{Cl}_3^a$	$\operatorname{Au}_{11}(\operatorname{PPh}_3)_6\operatorname{Cl}_3^b$	$[\mathrm{Au}_{11}(\mathrm{PPh}_3)_6\mathrm{Cl}_3]^{+a}$
-8.0	-22.0	-22.8
+107.9	+10.7	+72.8
-95.6	-7.6	-45.7
+4.3	-18.9	+4.3
	$\begin{array}{c} {\rm Au_{11}(PPh_3)_6Cl_3}^a\\ {\rm -8.0}\\ {\rm +107.9}\\ {\rm -95.6}\\ {\rm +4.3}\end{array}$	$Au_{11}(PPh_3)_6Cl_3^a$ $Au_{11}(PPh_3)_6Cl_3^b$ -8.0-22.0+107.9+10.7-95.6-7.6+4.3-18.9

<sup>*a*</sup>Results obtained in gas phase calculations. <sup>*b*</sup>Results obtained using PCM calculations. <sup>*c*</sup> $\Sigma \Delta E = \Delta E (\mathbf{Re} \rightarrow \mathbf{Im1}) + \Delta E (\mathbf{Im1} \rightarrow \mathbf{Im2}) + \Delta E (\mathbf{Im2} \rightarrow \mathbf{Re}).$ 

ACS Paragon Plus Environment



**Figure 4**. The atomic distances in the case of neutral  $Au_{11}(PPh_3)_6Cl_3$  are as follows, a = 0.75 and 0.75, b = 2.57 and 2.62, c = 0.82 and 1.83, and d = 2.01 and 1.04 Å in gas phase and PCM calculations, respectively. The atomic distances obtained in the case of positively charged cluster  $[Au_{11}(PPh_3)_6Cl_3]^+$  in gas phase calculations are a = 0.75, b = 2.57, c = 1.76, and d = 1.05 Å. The  $Au_{11}(PPh_3)_6Cl_3$  species was drawn in the space-filling mode according to the crystal structure of the  $Au_{11}(PPh_3)_7Cl_3$  cluster.<sup>27</sup> Color code: Au, green; P, purple; Cl, cyan. All the carbon and hydrogen atoms are omitted for clarity.

is +107.9 kcal/mol in the gas phase. This means that solvation can facilitate the elongation of the H—H bond (*c* in Figure 4) to produce charged species (NH<sub>4</sub><sup>+</sup> and H<sup>-</sup>). This is followed by reduction of protonated benzaldehyde to benzyl alcohol via an exothermic step by 95.6 and 7.6 kcal/mol in the gas phase and PMC calculations, respectively (Im2  $\rightarrow$  Re). A big difference between the PMC and the gas phase results is expected since reactants (Au<sub>11</sub>(PPh<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>—H<sup>-</sup> and PhCHO—NH<sub>4</sub><sup>+</sup>) are charged, hence become more stabilized in water compared to neutral products (Au<sub>11</sub>(PPh<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> and PhCH<sub>2</sub>OH—NH<sub>3</sub>).

We briefly pause here for perspective. The ESI-MS results indicate that removal of a phosphine ligand from clusters Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> and Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> result in the formation of  $[Au_{11}(PPh_3)_6Cl_3]^+$  and  $Au_{11}(PPh_2Py)_6Br_3$ , respectively. Note that the former one carries charge of +1, while the latter one is neutral. We think this is mainly due to the protection of the open metal site (Au2, Scheme 1C) by the lone-pair on nitrogen (Py) of the nearby ligands PPh<sub>2</sub>Py (Scheme 2, Re2). Coordination of Au2 site with the nitrogen leads to stabilization of molecular orbitals of the Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>6</sub>Br<sub>3</sub> cluster which in turn prevents oxidation of the cluster. In the case of  $Au_{11}(PPh_3)_6Cl_3$ , the open metal site (Au2) is easily accessible by solvents which may result in the oxidation of the cluster to form  $[Au_{11}(PPh_3)_6Cl_3]^+$ . In view of the protic nature of the solvents studied in the present work, gold oxidation by H<sup>+</sup> is prudent to consider. Although the redox potential  $(E_0)$  for such reaction is not high enough for spontaneous oxidation of gold,  $E_0$  decreases significantly for gold clusters compared to bulk Au. This is mainly due to nonlinear relationship between cluster size and  $E_0$ .<sup>48,4</sup>

In order to account the oxidation state of the cluster in the hydrogenation reaction, we performed DFT calculations on  $[Au_{11}(PPh_3)_6Cl_3]^+$  cluster in gas phase. The calculated change in energy ( $\Delta E$ ) for different steps of the proposed mechanism in Figure 4 are given in Table 2. Comparison of such energetics and inter-atomic distances (Figure 4) for  $Au_{11}(PPh_3)_6Cl_3$  and  $[Au_{11}(PPh_3)_6Cl_3]^+$  reveals that oxidation of the cluster can facilitate the activation of the H–H bond (*c* in Figure4) to produce charged species ( $NH_4^+$  and H<sup>-</sup>) in gas phase ( $Re \rightarrow Im1 \rightarrow Im2$ ). However, reduction of the aldehyde to alcohol seems to be less favorable when  $[Au_{11}(PPh_3)_6Cl_3]^+$  is used ( $Im2 \rightarrow Im2$ ).

**Re**). This must be more significant if solvation effect is taken into account. Since charged reactant (PhCHO-NH<sub>4</sub><sup>+</sup>) is considerably smaller than charged product ( $[Au_{11}(PPh_3)_6Cl_3]^+$ ), we expect the reactant becomes more stabilized than the products in water. Note that Born solvation free energy,  $\frac{1}{2}(1-1/\varepsilon)e^2/a$ , is inversely proportional to the ion diameter 2a( $\varepsilon$  and e are solvent dielectric constant and elementary charge, respectively). As a result, the **Im2**  $\rightarrow$  **Re** step in a polar solvent like H<sub>2</sub>O becomes less exothermic compared to the gas phase.

On the basis of the experimental and DFT results on natural and charged  $Au_{11}(PPh_3)_6Cl_3$ , we further propose a mechanism for the catalytic hydrogenation reaction catalyzed by  $Au_{11}(PPh_2Py)_7Br_3$  (Scheme 2). At the first step, one PPh\_2Py ligand is removed from Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>Br<sub>3</sub> to yield Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>6</sub>Br<sub>3</sub> species. This step exposes a gold atom to the reactants (e.g., aldehyde and H<sub>2</sub>). Then, H<sub>2</sub> adsorbs onto the open metal site with subsequent activation of the H-H bond with the help of pyridine group of phosphine ligands on Au clusters. The pyridine group abstracts a proton from H<sub>2</sub> to form pyridinium (PyH<sup>+</sup>), leaving H<sup>-</sup> on the core (Au2 site) for the ensuing hydrogenation (Scheme 2, Step I). Similar proton transfer was indeed found in the case of gold nanoparticle protected by functional ligand P(Naph)(<sup>*t*</sup>-Bu)OH where the H<sub>2</sub> was activated on gold with the help of -OH group of the phosphine ligand.<sup>26</sup> Next, nitrobenzaldehyde gets physically absorbed on the surface of the cluster via interactions of -CHO groups with PyH<sup>+</sup> and H<sup>-</sup> (Scheme 2, Step II). Finally,  $H^+$  (PyH<sup>+</sup>) and H<sup>-</sup> will be transferred to NO<sub>2</sub>PhCHO to produce NO<sub>2</sub>PhCH<sub>2</sub>OH product (Scheme 2, Step III).



**Scheme 2**. The  $Au_{11}(PPh_2Py)_7Br_3$  and  $Au_{11}(PPh_2Py)_6Br_3$  species was drawn in the space-filling mode according to the crystal structure of the  $Au_{11}(PPh_3)_7Br_3$  cluster.<sup>41</sup> Color code: Au, green; P, purple; Br, cyan. Ph\_2Py of other phosphine ligands are omitted for clarity.

## ■ CONCLUSIONS

We report a facile one-pot synthesis of the functionalized ligand-protected gold cluster formulated as  $Au_{11}(PPh_2Py)_7Br_3$ . The as-prepared gold cluster is well-determined by UV-vis spectroscopy and electrospray ionization mass spectrometry. The CeO<sub>2</sub>-supported cluster catalyst shows good catalytic performance, including activity and selectivity in the chemoselective hydrogenation of nitrobenzaldehyde in the absence of amine base. A perfect 100% selectivity for the nitrobenzyl alcohol is observed. ESI-MS, UV-vis, and DFT results indicate that one ligand removal is the key step to activate gold clusters toward reactants. The protecting functionalized ligand, diphenyl-2-pyridylphosphine, plays a crucial role in the catalytic hydrogenation. In all, this study gives a cue to design and develop better and environmentally friendly nanogold catalysis for use in the chemical industry.

#### ASSOCIATED CONTENT

**Supporting Information.** The experimental and simulated isotopic distribution patterns of species  $[Au_{11}(PPh_2Py)_7Br_3Cs_1]^+$ ,  $[Au_{11}(PPh_2Py)_7Br_3Cs_2]^{2+}$ , and  $[Au_{11}(PPh_3)_6Cl_3Cs]^{2+}$ , recovery and reuse of the  $Au_{11}(PPh_2Py)_7Br_3/CeO_2$  catalyst, and FT-IR spectra of  $Au_{11}(PPh_2Py)_7Br_3/CeO_2$  catalyst before and after the thermal treatment. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

## AUTHOR INFORMATION

#### **Corresponding Author**

\*Email: gaoli@dicp.ac.cn

#### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENT

G.L. acknowledges financial support by the starting funds of the Dalian Institute of Chemical Physics and the "Thousand Youth Talents Plan".

#### REFERENCES

- (1) Yau, S.; Varnavski, O.; T. Goodson, III, Acc. Chem. Res. 2013, 46, 1506–1516.
  - (2) Lu, Y.; Chen, W. Chem. Soc. Rev. 2012, 41, 3594–3623.
- (3) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. Acc. Chem. Res. 2001, 34, 181–190.
- (4) Schmid, G.; Bäumle, M.; Geerkens, M.; Heim, I.; Osemann, C.; Sawitowski, T. *Chem. Soc. Rev.* **1999**, *28*, 179–185.
  - (5) Häkkinen, H. Nature Chem. 2012, 4, 443-455.
  - (6) Jin, R. Nanoscale 2010, 2, 343-362.
- (7) Shenhar, R.; Norsten, T. B.; Rotello, V. M. Adv. Mater. 2005, 17, 657–669.
- (8) Vignolle, J.; Tilley, T. D. Chem. Commun. 2009, 46, 7230–7232.
- (9) Aslam, M.; Fu, L.; Su, M.; Vijayamohanan, K.; Dravid, V. P. J. Mater. Chem. 2004, 14, 1795–1797.

(10) Maity, P.; Tsunoyama, H.; Yamauchi, M.; Xie, S.; Tsukuda, T. J. Am. Chem. Soc. 2011, 133, 20123–20125.

- (11) Li, G.; Jin, R. J. Am. Chem. Soc. 2014, 136, 11347-11354.
- (12) Wan, X.; Yuan, S.; Lin, Z.; Wang, Q. Angew. Chem. Int. Ed. 2014, 53, 2923–2926.
- (13) Shichibu, Y.; Negishi, Y.; Watanabe, T.; Chaki, N. K.; Kawaguchi, H.; Tsukuda, T. J. Phys. Chem. C 2007, 111, 7845–7847.
- (14) Mathew, A.; Natarajan, G.; Lehtovaara, L.; Hakkinen, H.; Kumar, R. M.; Subramanian, V.; Jaleel, A.; Pradeep, T. *ACS Nano* **2014**, *8*, 139–152.
- (15) Kawasaki, H.; Kumar, S.; Li, G.; Zeng, C.; Kauffman, D.; Yoshimoto, J.; Iwasaki, Y.; Jin, R. *Chem. Mater.* **2014**, *26*, 2777–2788.
- (16) Chen, L.; Wang, C.; Yuan, Z.; Chang, H. Anal. Chem. 2015, 87, 216–229.
  - (17) Taketoshi, A.; Haruta, M. Chem. Lett. 2014, 43, 380-387.
  - (18) Li, G.; Jin, R. Acc. Chem. Res. 2013, 46, 1749-1758.
- (19) Yamazoe, S.; Koyasu, K.; Tsukuda, T. Acc. Chem. Res. 2014, 47, 816–824.
- (20) Li, G.; Zeng, C.; Jin, R. J. Am. Chem. Soc. 2014, 136, 3673–3679.
- (21) Li, G.; Jiang, D.; Liu, C.; Yu, C.; Jin, R. J. Catal. 2013, 306, 177–183.

(22) Gorin, D. J.; Sherry, B. D.; Toste, F. D. Chem. Rev. 2008, 108, 3351–3378.

(23) Li, G.; Jiang, D.; Kumar, S.; Chen, Y.; Jin, R. ACS Catal. 2014, 4, 2463–2469.

(24) Cano, I.; Chapman, A. M.; Urakawa, A.; van Leeuwen, P. J. Am. Chem. Soc. 2014, 136, 2520–2528.

(25) Yan, M.; Jin, T.; Ishikawa, Y.; Minato, T.; Fujita, T.; Chen, L.; Bao, M.; Asao, N.; Chen, M.; Yamamoto, Y. J. Am. Chem. Soc. **2012**, *134*, 17536–17542.

(26) Gaussian 09, Revision D.01, 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, N. J.; 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, Inc., Wallingford CT, 2009.

- (27) Becke, A. D. Phys. Rev. A 1988, 38, 3098-3100.
- (28) Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652.
- (29) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671–6687.
  - (30) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 270-283.
- (31) Assadollahzadeh, B.; Schwerdtfeger, P. J. Chem. Phys. 2009, 131, 064306.
- (32) Lyalin, A.; Taketsugu, T. J. Phys. Chem. Lett. 2010, 1, 1752–1757.
- (33) Faza, O. N.; Rodríguez, R. Á.; López, C. S. *Theor. Chem. Acc.* **2011**, *128*, 647–661.
- (34) Zubarev, D. Y.; Boldyrev, A. I. J. Phys. Chem. A 2009, 113, 866–868.
- (35) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. J. Comp. Chem. **2001**, *22*, 976–984.
- (36) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; De-Frees, D. J.; Pople, J. A.; Gordon, M. S. *J. Chem. Phys.*, **1982**, *77*, 3654–3665.
- (37) Fuentealba, P.; Preuss, H.; Stoll, H.; Szentpály, L. V. Chem. Phys. Lett. **1982**, 89, 418-422.
- (38) Igel-Mann, G.; Stoll, H.; Preuss, H. Mol. Phys. 1988, 65, 1321–1328.
- (39) Scalmani, G.; Frisch, M. J. J. Chem. Phys. 2010, 132, 114110.
  (40) McKenzie, L. C.; Zaikova, T. O.; Hutchison, J. J. Am. Chem.
- Soc. 2014, 136, 13426–13435. (41) Gutrath, B. S.; Englert, U.; Wang, Y.; Simon, U. Eur. J. In-
- (41) Gutrath, B. S.; Englert, U.; Wang, Y.; Simon, U. Eur. J. Inorg. Chem. **2013**, *12*, 2002–2006.
- (42) Lin, J.; Li, W.; Liu, C.; Huang, P.; Zhu, M.; Ge, Q.; Li, G. *Nanoscale* **2015**, *7*, 13663–13670.
- (43) Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. F.; Whitehouse, C. M. Science **1989**, 246, 64–71.
- (44) Wu, Z.; Jiang, D.; Mann, A. K. P.; Mullins, D. R.; Qiao, Z.; Allard, L. F.; Zeng, C.; Jin, R.; Overbury, S. H. J. Am. Chem. Soc. **2014**, *136*, 6111–6122.
- (45) Elliott, III, E. W.; Glover, R. D.; Hutchison, J. E. ACS Nano 2015, 9, 3050–3059.
- (46) Yoskamtorn, T.; Yamazoe, S.; Takahata, Y.; Nishigaki, J.; Thivasasith, A.; Limtrakul, J.; Tsukuda, T. *ACS Catal.* **2014**, *4*, 3696– 3700.
- (47) Lopez-Acevedo, O.; Kacprzak, K. A.; Akola, J.; Häkkinen, H. *Nature Chem.* **2010**, *2*, 329–334.
- (48) Carrettin, S.; Guzman, J.; Corma, A. Angew. Chem. Int. Ed. 2005, 44, 2242–2245.
- (49) Zhou, Z.; Liu, M.; Wu, X.; Yu, H.; Xu, G.; Xie, Y. Appl. Organometal. Chem. **2013**, *27*, 562–569.

TOC Au<sub>11</sub>(PPh<sub>2</sub>Py)<sub>7</sub>X<sub>3</sub>: H<sub>2</sub>

