

# Synthesis, single crystal X-ray analysis, and TEM for a single-sized Au<sub>11</sub> cluster stabilized by SR ligands: The interface between molecules and particles

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## Abstract

An SR-modified Au cluster with a sub-nanometer size, Au<sub>11</sub>(S-4-NC<sub>5</sub>H<sub>4</sub>)<sub>3</sub>(PPh<sub>3</sub>)<sub>7</sub> (**1**), has been synthesized by NaBH<sub>4</sub> reduction of Au(S-py)(PPh<sub>3</sub>) or by reacting [Au<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>](NO<sub>3</sub>)<sub>3</sub> with HS-4-py in good yield. Its molecular structure has been elucidated by single crystal X-ray diffraction, and TEM observation has been achieved for the first time for this size of SR-modified Au clusters. The core structure is best described in terms of an incomplete icosahedron. CV measurements in CH<sub>2</sub>Cl<sub>2</sub> have suggested that the cluster does not coagulate in solution with significant concentration.

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## 1. Introduction

For the past decade much attention has been devoted to the synthesis of nanoparticles with a narrow core size distribution by the use of SR modification techniques in order to protect and/or to stabilize Au nanoparticles, including colloids, from agglomeration [1]. In order to obtain single-sized sub-nanoparticles, highly elaborate fine separation procedures are needed after synthesis [2], and the yields are very poor. The generally accepted concept behind this modification comes from the implicit contention that the original structure of gold particles is sustained after the introduction of protecting SR ligands [1]. However, there

have been only limited reports regarding the structural elucidation of SR-modified Au molecular clusters to support this hypothesis [3]. The chemistry therefore remains a contentious issue. Indeed, two contradictory results have thus far been reported, that is, the case of simple substitution of the SR groups for the ligand to be replaced where the original structure around the relevant gold atoms is sustained after the reaction, and the other case where complete structural change occurs after treatment with SR ligand. From the perspective of nanoparticle synthesis, we have begun a systematic exploration of the modification of Au(I) molecules by SR ligand(s). Here, we report the first synthesis of an SR-modified Au<sub>11</sub> molecular cluster, Au<sub>11</sub>(S-4-NC<sub>5</sub>H<sub>4</sub>)<sub>3</sub>(PPh<sub>3</sub>)<sub>7</sub> (**1**), in a preparative scale as well as single crystal and TEM structural elucidation, which should serve as a structural model for such sub-nanometer sized gold particles with SR ligands; the TEM image of this cluster is the

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smallest one ever observed [4]. In addition, this paper provides a new vista for  $\text{Au}_{11}$  molecular clusters reported thus far with the general formula  $\text{Au}_{11}(\text{PR}_3)_7\text{X}_3$  ( $\text{X} = \text{halogen}, \text{SCN}, \text{CN}$ ) [5], by virtue of the potential use of this cluster as a building block for constructing larger Au molecular clusters [6], as our  $\text{Au}_{11}$  cluster has three dangling S-py ligands.

## 2. Synthesis

$\text{Au}_{11}(\text{S-4-NC}_5\text{H}_4)_3(\text{PPh}_3)_7$  (**1**) has been synthesized by two different routes, both in practical yields. The first is the reductive condensation of the mononuclear Au(I) derivative,  $\text{Au}(\text{S-py})(\text{PPh}_3)$  (**2**) ( $\text{S-py} = \text{S-4-NC}_5\text{H}_4$ ) [7], by  $\text{NaBH}_4$  in 25% yield on the basis of single crystals; an equimolar amount of **2** and  $\text{NaBH}_4$  were mixed in an alcohol with stirring and work-up, and recrystallization from  $\text{CH}_2\text{Cl}_2$ –ethanol–hexane afforded scarlet single crystals of **1**. The yield for the powder product was better than 25% and is close to that of the second method described below. Most of the  $\text{Au}_{11}$  clusters described in the Introduction have been synthesized by this reduction method of mononuclear  $\text{AuPR}_3\text{X}$  ( $\text{X} = \text{halogen}, \text{SCN}, \text{CN}$ ) [5]. Cluster **1** was also synthesized by treating  $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_3$  (**3**) [5c] with HS-4-py/MeOH–KOH in a 70% yield (solid product). Single crystals were obtained in 42% yield. This synthetic process via a  $\text{Au}_9$  cluster is one of the established methods for preparing  $\text{Au}_{11}$  clusters [8]. Although the apparent yield for the first method is rather low, products other than **1**

have not been isolated and/or identified by this reduction reaction.

## 3. Structural determination and bondings

Fig. 1 shows the molecular structure of **1** clarified by use of a small single crystal with a synchrotron radiation source. The  $\text{Au}_{11}$  core structure is quite similar to that of  $\text{Au}_{11}\text{Cl}_3\{\text{P}(\text{3-CF}_3\text{-C}_6\text{H}_4)_3\}_7$  [9] and to those of  $\text{Au}_{11}\text{X}_3(\text{PR}_3)_7$  [5a,5b], both of which have incomplete icosahedral skeletons with an approximately  $C_{3v}$  symmetry axis. The main geometrical parameters of **1** are as follows:  $r(\text{Au}(\text{center})\text{–Au}(\text{peripheral})) = 2.6295\text{–}2.7185 \text{ \AA}$ , and  $r(\text{Au}(\text{peripheral})\text{–Au}(\text{peripheral})) = 3.0611\text{–}3.2693 \text{ \AA}$ , which are longer than those of halogen analogues. The Au–S distances in **1** are 2.336–2.337 Å, which are significantly longer than those of mononuclear Au(I) derivatives (2.29(1)–2.318(3) Å), and the Au–P distances 2.272–2.285 Å are also slightly longer than those for mononuclear derivatives, (2.215(6)–2.28(1) Å) [7]. These findings indicate that the skeletal expansion of **1** occurs upon introduction of S-py ligands. Selected bond lengths and angles are given in Table 1.

The TEM image (Fig. 2) clearly exhibits particles with diameters less than 1 nm. Since the size of the Au core of **1** is approximately 0.6 nm, the particles shown should reflect the metal core of **1**, which is maintained under TEM measurements. As it is quite difficult to obtain clear TEM images for nanoparticles this small in size, to our knowledge, the image of **1** reflects one of the smallest par-

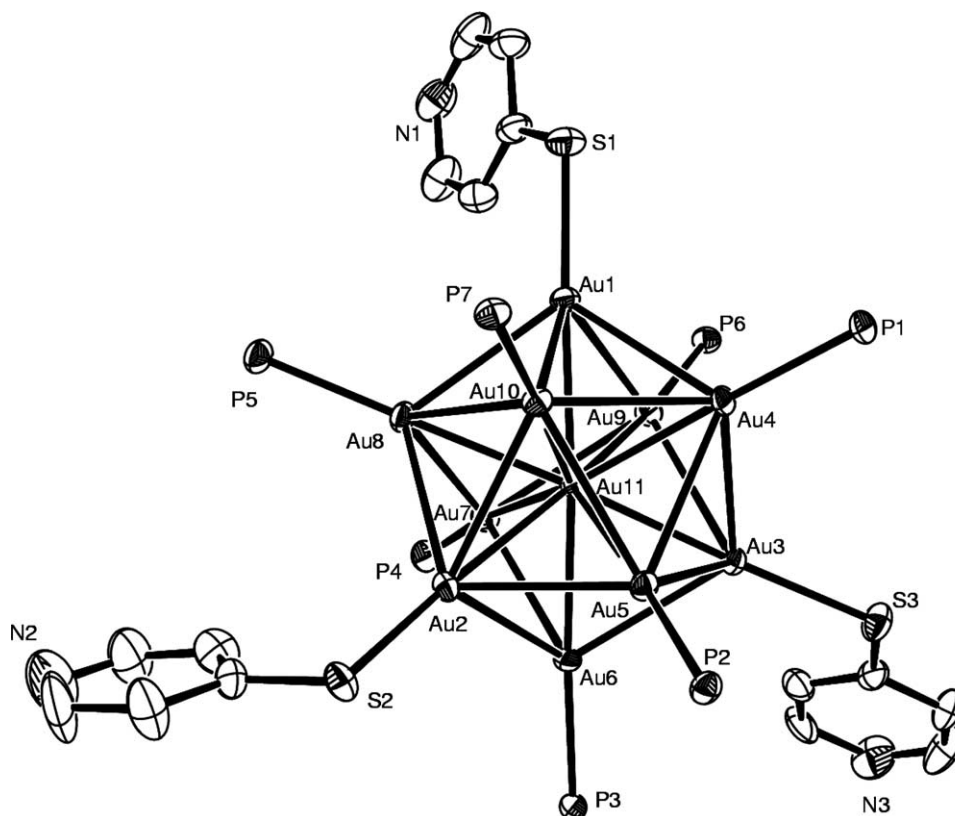


Fig. 1. The core molecular structure of **1**. Phenyl groups in  $\text{PPh}_3$  are omitted for clarity.

Table 1  
Selected bond lengths (Å) and angles (°)

Au1–Au1	2.7184(5)	Au11–Au2	2.6991(5)	Au11–Au3	2.7066(5)
Au11–Au4	2.6834(5)	Au11–Au5	2.6890(4)	Au11–Au6	2.6496(5)
Au11–Au7	2.6294(5)	Au11–Au8	2.6546(5)	Au11–Au9	2.6427(5)
Au11–Au10	2.6710(5)	Au1–Au4	2.9225(5)	Au1–Au8	2.9214(6)
Au1–Au9	2.8806(5)	Au1–Au10	2.8950(5)	Au2–Au5	2.8567(6)
Au2–Au6	2.9247(5)	Au2–Au8	2.8949(5)	Au2–Au10	3.0414(5)
Au3–Au4	2.8450(5)	Au3–Au5	3.0051(5)	Au3–Au6	2.8525(6)
Au3–Au9	2.9471(5)	Au4–Au5	3.0335(5)	Au4–Au9	3.2693(5)
Au4–Au10	2.9549(5)	Au5–Au6	3.1219(5)	Au5–Au10	2.9804(5)
Au6–Au7	2.9183(5)	Au7–Au8	2.9300(5)	Au7–Au9	2.9621(6)
Au8–Au10	3.0612(5)	Au1–S1	2.337(3)	Au2–S2	2.336(3)
Au3–S3	2.335(3)	Au4–P1	2.272(3)	Au5–P2	2.285(2)
Au6–P3	2.276(3)	Au7–P4	2.283(3)	Au8–P5	2.274(3)
Au9–P6	2.272(2)	Au10–P7	2.275(2)		
Au1–Au11–Au2	121.18(2)	Au1–Au11–Au3	115.96(2)	Au1–Au11–Au4	65.50(1)
Au1–Au11–Au5	123.34(2)	Au1–Au11–Au6	164.74(2)	Au1–Au11–Au7	98.47(2)
Au1–Au11–Au8	65.86(1)	Au1–Au11–Au9	64.98(1)	Au1–Au11–Au10	64.98(1)
Au2–Au11–Au3	118.76(2)	Au2–Au11–Au4	124.36(2)	Au2–Au11–Au5	64.04(1)
Au2–Au11–Au6	66.29(1)	Au2–Au11–Au7	91.54(2)	Au2–Au11–Au8	65.46(1)
Au2–Au11–Au9	159.90(2)	Au2–Au11–Au10	68.99(1)	Au3–Au11–Au4	63.72(1)
Au3–Au11–Au5	67.69(1)	Au3–Au11–Au6	64.35(1)	Au3–Au11–Au7	100.45(1)
Au3–Au11–Au8	167.63(2)	Au3–Au11–Au9	66.85(1)	Au3–Au11–Au10	122.07(2)
Au4–Au11–Au5	68.76(1)	Au4–Au11–Au6	123.12(2)	Au4–Au11–Au7	144.09(2)
Au4–Au11–Au8	124.89(2)	Au4–Au11–Au9	75.73(2)	Au4–Au11–Au10	66.99(1)
Au5–Au11–Au6	71.57(1)	Au5–Au11–Au7	137.88(2)	Au5–Au11–Au8	122.49(2)
Au5–Au11–Au9	131.08(2)	Au5–Au11–Au10	67.57(1)	Au6–Au11–Au7	67.12(1)
Au6–Au11–Au8	110.42(2)	Au6–Au11–Au9	103.44(2)	Au6–Au11–Au10	128.93(2)
Au7–Au11–Au8	67.35(1)	Au7–Au11–Au9	68.37(1)	Au7–Au11–Au10	137.48(2)
Au8–Au11–Au9	105.16(2)	Au8–Au11–Au10	70.17(1)	Au9–Au11–Au10	126.32(2)
S1–Au1–Au11	175.40(7)	S2–Au2–Au11	174.77(7)	S3–Au3–Au11	173.25(7)
P1–Au4–Au11	173.05(7)	P2–Au5–Au11	176.04(7)	P3–Au6–Au11	176.42(7)
P4–Au7–Au11	173.39(7)	P5–Au8–Au11	178.07(7)	P6–Au9–Au11	173.66(7)
P7–Au10–Au11	174.15(7)	Au1–S1–C11	106.6(4)	Au2–S2–C21	108.3(4)
Au1–S3–C31	109.4(4)				

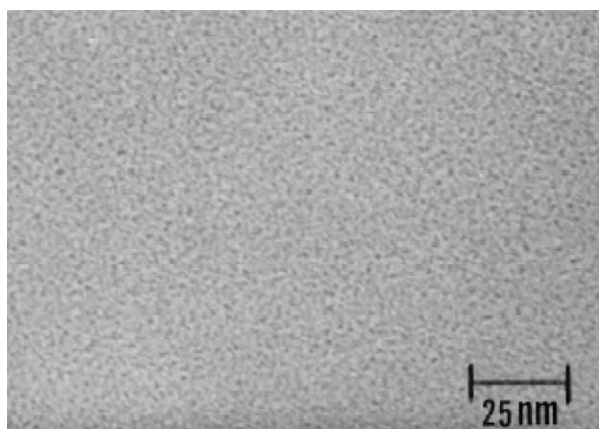


Fig. 2. The TEM image of **1** at  $2 \times 10^5$  magnification.

ticles observed thus far by this method [2,4,10–12]; the size of the smallest cluster particles made thus far by TEM image measurements is approximately 1.0 nm [2,4,12]. Cluster **1** should be stabilized by anchoring to the substrate surface via a pyridine N atom and prevented from agglomeration under the conditions of the TEM observation.

The XPS spectrum of **1** for Au 4f electrons was subjected to curve-fitting, which resulted in three distinct peaks, that is, seven peripheral gold atoms bound to

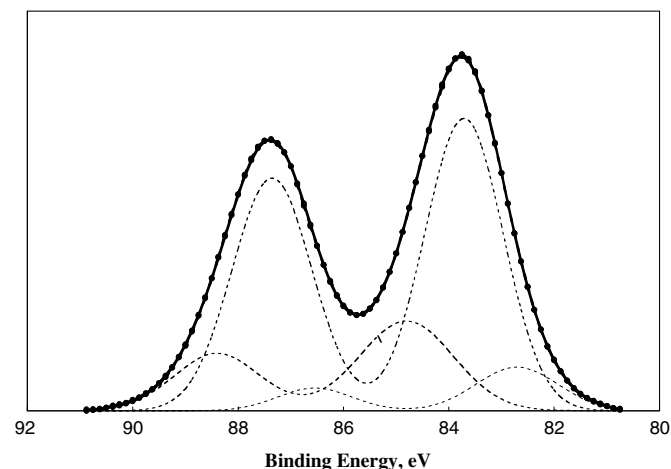


Fig. 3. XPS spectrum of **1** at 4f electron level: (●) represents the observed spectrum; (—) simulated spectrum; (---) resolved spectra.

$\text{PPh}_3$ , three peripheral gold atoms bound to S-py, and one central gold atom (Fig. 3). The peak assigned to the three peripheral gold atoms is centered at 84.8 eV, that to the seven peripheral gold atoms at 83.8 eV, and that to the central gold atom at 82.8 eV for  $4f_{7/2}$  levels. All these peaks are slightly shifted to lower energies compared with the relevant  $\text{Au}_{11}$  molecular clusters described

above [9,13–16]. These lower energy shifts suggest that the positive electron density for each gold atom is reduced to some extent by substituting S-py groups for halogen ligands in  $\text{Au}_{11}\text{Cl}_3\text{-}\{\text{P}(\text{3-CF}_3\text{-C}_6\text{H}_4)_3\}_7$  and  $\text{Au}_{11}\text{X}_3(\text{PR}_3)_7$ .

#### 4. CV measurement

CV measurements of **1** in  $\text{CH}_2\text{Cl}_2$  exhibited an irreversible oxidation potential at  $-0.397\text{ V}$  and its reversed reduction potential at  $-1.060\text{ V}$  (versus  $\text{Ag}|\text{Ag}^+$ ) (Fig. 4, supplementary material). It is well known that Au nanoparticles composed of larger numbers of gold atoms exhibit several steps of successive one-electron redox waves [17–19]. Quinn et al. [20] have also reported 15 evenly spaced peaks for hexanethiol-capped  $\text{Au}_{147}$  particles as well as several peaks for  $\text{Au}_{38}$  clusters. These results are interpreted in terms of quantized double-layer charging. The redox data for **1** strongly suggest that the electrochemical behavior of **1** is characteristic of a molecule in solution at considerable concentration.

#### 5. S-py modification reactions of other Au derivatives

It is quite intriguing to determine if our methods for SR modification in Au-halogen clusters are generally valid. To make this determination, 4-S- $\text{CH}_2$ -py was employed instead of S-py in the substitution reaction of 4-S-R-py for Cl in  $\text{Au}(\text{Cl})\{\text{P}(\text{2-py})\text{Ph}_2\}$  (**4**). However, the mononuclear starting complex **4** was changed to trinuclear  $\{\text{S}[\text{Au}\{\text{P}(\text{2-py})\text{Ph}_2\}]_3\}\text{Cl}$  (**5**), which suggests that the core structure is not guaranteed upon substitution. Treatments of  $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_3$  (**3**) with 4-S- $\text{CH}_2$ -py and/or 4-S- $\text{CH}_2\text{-CH}_2$ -py/MeOH-KOH did not afford desired clusters. Thus, direct substitution of SR for X in  $\text{Au}_{11}\text{X}_3(\text{PR}_3)_7$  is more attractive and relevant to the burgeoning field of SR modification of gold nanoparticles. IR spectra for the reaction product of  $\text{Au}_{11}\text{I}_3(\text{PPh}_3)_7$  (**6**) with S-py indicate that the simple substitution of S-R groups for I in **6** is likely with retention of the original structure. It has also been shown from IR and XPS spectra that the reaction of  $\text{Au}_{11}\text{Cl}_3\{\text{P}(\text{3-CF}_3\text{-C}_6\text{H}_4)_3\}_7$  (**7**) [9] with S-py results in retention of the original structure upon substitution of S-R groups for Cl in **7**. However, attempts to insert- $\text{CH}_2$ -group(s) between S and the pyridine ring, that is, 4-S- $\text{CH}_2$ -py and 4-S- $\text{CH}_2\text{-CH}_2$ -py, in order to contribute to the current chemistry of SR modification of gold nanoparticles with a longer alkyl chain, have not been successful because of the destruction of  $\text{Au}_{11}$  skeleton in **7**. These results strongly suggest that the size or shape of the original Au cluster is not necessarily guaranteed after the treatment by SR, where R is a longer alkyl chain, and indicate that results should be carefully assayed by modifying Au nanoparticles with SR ligands [1,3].

It is worthwhile to mention that the pyridine N atom in the dangling S-py ligand is capable of coordinating to an-

other metal center to create supramolecular assemblies. The fundamental effectiveness of this strategy was verified in our recent study [6], in which a series of  $[\text{M}(\text{acac}')_2(\text{py-4-S-AuPR}_3)_2](\text{ClO}_4)_x$  supramolecules was successfully synthesized by the use of mononuclear  $\text{Au}(\text{S-4-py})\text{PR}_3$  complex as building blocks. Cluster **1** has three dangling S-py ligands. Therefore, it is highly probable that a tailored synthesis of higher nuclearity Au clusters with a non-magic number on other metal scaffolding(s) can be achieved by employing **1** as a  $\text{Au}_{11}$  fundamental unit. Our efforts in this regard are continuing.

#### 6. Concluding remarks

Mass spectroscopic techniques have thus far been primarily employed for characterizing nanoparticles because of difficulties in obtaining TEM images for such small nano-particles [3]. An important contribution of the present study to nanotechnology has been to clarify the structural understanding of SR-modified Au nanoparticles by offering structural details of molecular cluster **1** based on single crystal X-ray structural analysis and TEM measurements. Thus a deeper structural understanding of Au nanoparticles has made it possible to explore the inner structures of such compounds. Another important contribution has been to provide simple synthetic procedures for preparing perfect single-sized Au particles of less than 1 nm on a practical scale.

#### 7. Experimental

##### 7.1. Synthesis

Reactions were carried out under an argon atmosphere by standard Schlenk techniques. The reaction vessel was covered with a piece of black cloth.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum was recorded on a Varian XL-200 spectrometer at 80.984 MHz. The chemical shift is referenced to external 85%  $\text{H}_3\text{PO}_4$ .

##### 7.1.1. $\text{Au}_{11}(\text{S-4-NC}_5\text{H}_4)_3(\text{PPh}_3)_7$ (**1**)

7.1.1.1. Method (a). To an ethanol solution (80 mL) of  $\text{Au}(\text{S-4-py})\text{PPh}_3$  (570 mg, 1.0 mmol),  $\text{NaBH}_4$  (40 mg, 1.0 mmol) was added, and the mixture was stirred at room temperature for 4 h. The mixture was left standing at room temperature for 3 days. The resulting scarlet precipitates were collected by filtration and dissolved in  $\text{CH}_2\text{Cl}_2$ . To this was added ethanol and then hexane to give scarlet single crystals of **1** (98 mg, 25% as single crystals). Found: C, 38.94; H, 2.75; N, 0.96%.  $\text{C}_{141}\text{H}_{117}\text{N}_3\text{Au}_{11}\text{P}_7\text{S}_3$  requires C, 39.08; H, 2.72; N, 0.97%.  $^{31}\text{P}$  NMR (200 MHz; solvent  $\text{CDCl}_3$ ; standard  $\text{H}_3\text{PO}_4$ );  $\delta$  50.45 (s).  $\lambda_{\text{max}}/\text{nm}$  ( $\text{CH}_2\text{Cl}_2$ ) 258, 304, 430.

7.1.1.2. Method (b). Thirty-three milligram (0.3 mmol) of 4-py-SH and 18 mg (0.3 mmol) of KOH were dissolved into 20 mL of ethanol. This solution was added to an ethanol solution (10 mL) of  $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_3$  (**3**) (203 mg,

0.05 mmol), and the mixture was stirred at room temperature for several hours. After standing at room temperature for a week, the resulting scarlet precipitates were recrystallized as above to give single crystals of **1** (74 mg, 42%).

### 7.2. X-ray crystallography

Selected crystals of **1** were attached to a nylon loop for low-temperature measurements. The reflection data were collected by a MAC Science DIP-LABO imaging plate diffractometer installed in the BL04B2 beamline of the SPring-8 synchrotron facility ( $\lambda = 0.3282 \text{ \AA}$ ) [21]. Crystal data: **1**;  $C_{141}H_{117}Au_{11}N_3P_7S_3 \cdot EtOH \cdot (H_2O)_2$ ,  $M = 4415$ , triclinic,  $P\bar{1}$ ,  $a = 16.142(1) \text{ \AA}$ ,  $b = 17.354(1) \text{ \AA}$ ,  $c = 27.803(1) \text{ \AA}$ ,  $\alpha = 94.25(1)^\circ$ ,  $\beta = 98.17(1)^\circ$ ,  $\gamma = 98.96(1)^\circ$ ,  $Z = 2$ ,  $V = 7578.5(7) \text{ \AA}^3$ ,  $\mu = 1.463 \text{ mm}^{-1}$ ,  $D_c = 1.899 \text{ g cm}^{-3}$ ,  $T = 120 \text{ K}$ . The structure was solved by direct methods using SIR-97 and SHELX-97 in the WINGX program package for 29,957 reflections with  $I_0 > 2\sigma(I_0)$  among 35,563 collected reflections [22]. The refinements were made on  $F^2$  data with anisotropic thermal parameters by full-matrix least-squares.  $R(wR_2) = 0.049 (0.12)$  for 1531 parameters. Tables of atomic coordinates, thermal parameters, and bond lengths and angles are available as supporting information (CCDC – 260895 (1)).

### 7.3. TEM and XPS measurements

TEM observation was carried using a Hitachi H-800 at 200 kV. Samples were put onto a carbon-coated copper grid [12]. The TEM image of **1** was taken at  $2 \times 10^5$  magnification.

XPS measurements were made on an ULVAC-PHI ESCA-5700MC spectrometer with Mg  $K\alpha$  exciting radiation (1253.6 eV), as described previously [9]. Finely ground powder samples of **1** and BN standard were pressed into a disk and the disk, was mounted on a stub. The  $4f_{7/2}$  and  $4f_{5/2}$  binding energies of Au(I) were calibrated versus the B 1s or N 1s lines of a sample base.

### 7.4. CV measurements

A cyclic voltammogram of **1** was taken for a 0.13 mM sample solution of  $CH_2Cl_2$  containing 0.1 M  $Bu_4NBF_4$ . A glassy carbon disk electrode (0.3 mm, o.d.) was employed, and the scanning speed was 0.2 V/s.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.09.043.

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