Synthesis and Characterization of the Au_{11} Cluster with Sterically Demanding Phosphine Ligands by Single Crystal X-ray Diffraction and XPS Spectroscopy

Keiko Nunokawa, Satoru Onaka,*
Tadashi Yamaguchi,† Tasuku Ito,†
Seiji Watase,†† and Masami Nakamoto††

Department of Environmental Technology, Graduate School of Engineering, Nagoya Institute Technology,
Gokiso-cho, Showa-ku, Nagoya 466-8555

†Department of Chemistry, Graduate School Science,
Tohoku University, Aoba-ku, Sendai 980-8578

††Osaka Municipal Technical Research Institute,
1-6-50, Morinomiya, Joto-ku, Osaka 536-8553

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A new Au_{11} cluster with (m-$CF_3C_6H_4$)$_3$P ligands has been synthesized and characterized by single crystal X-ray and XPS analysis. The cluster has an incomplete icosahedral skeleton similar to known $Au_{11}X_3(PR_3)_7$ clusters, but a stronger distortion from the ideal symmetry has been caused by introducing CF_3 substituents at a *meta*-position of each phenyl ring of PR_3 ligands.

A generally accepted strategy for fabricating higher-nuclearity Au clusters is the option of phosphine ligands.[1,2] In the previous paper, we described a simple idea to increase the steric demand of a phosphine ligand, and that is by the introduction of CF_3 substituent(s) into the *meta* or *para* position(s) of the phenyl rings in Ph_3P.[3] When the CF_3 substituent(s) was introduced into the *meta* position(s) of the phenyl rings for Ph_3P–Au–Cl, an unexpected effect of the CF_3 substituent on the Au–Au interaction (aurophilicity) was revealed.[3] Aurophilicity was induced even for this kind of simple halide phosphine derivative of Au(I). This had not been the case for similar Au(I) derivatives with bulky monodentate phosphine ligands.[4–6] As CF_3 is an electron-withdrawing substituent, the following query comes out immediately: which factor is more influential on the aurophilicity, the steric effect or the electronic effect? The previous paper also reported that the aurophilicity was not induced if the CF_3 substituent was introduced into the *para* position of each phenyl ring, where the electron-withdrawing effect is more accentuated.[3] That finding lends some support to the view that the steric effect is more operative on the aurophilicity, because the steric demand of the substituted triphenylphosphine ligand is increased by the expansion of the Tolman's cone angle[7] for *meta*-substitution. It is well recognized that the steric effect of the phosphine ligand is not only influential on the aurophilicity, but also on the nucreality and/or size of the resulting clusters.[1,2] This paper reports the synthesis of a new Au_{11} congener to $Au_{11}X_3(PR_3)_7$ (X = SCN, Cl, and I) (R = p-YC_6H_4 (Y = F or Cl or H)) clusters and the significant distortion of the peripheral gold atoms in the Au_{11} skeleton from those described above.[8]

$Au_{11}Cl_3\{(m\text{-}CF_3C_6H_4)_3P\}_7$ (**1**) was synthesized from (m-$CF_3C_6H_4$)$_3$P–Au–Cl with significant yield. Figure 1 shows the skeletal structure of molecule **1**. The core structure is quite similar to analogous Au_{11} clusters described above; an incomplete icosahedron is formed in which one triangular face has been substituted by a single gold atom Au(11). Although the crystal belongs to the monoclinic space group $P2_1/n$, the molecule possesses a pseudo C_3 axis along the Au(1)–Au(11) bond.[8a] The core Au(1) atom is surrounded by ten gold atoms and the relevant bond lengths are in the range 2.6265(6)–2.7107(7) Å, the mean of ten values being 2.679 Å, which is very close to the corresponding mean value found in $Au_{11}I_3\{(p\text{-}FC_6H_4)_3P\}_7$ (2.68 Å).[8a] The peripheral Au–Au bond lengths are in the range 2.8264(8)–3.3178(7) Å, the mean of twenty-one values being 2.978 Å, which is very close to that of the corresponding iodide (2.98 Å).[8a] However, three Au–Au interactions among twenty-one are considerably lengthened with respect to the remaining peripheral Au–Au bonds and the difference in three pairs of Au–Au interactions is significant. The Au(4)–Au(8) bond 3.0043(6) Å is the shortest, the Au(2)–Au(7) bond is 3.1257(7) Å and the Au(5)–Au(10) 3.3178(7) Å is the longest. The relevant three Au atoms to these bonds (Au(2), Au(4), and Au(5)) constitute the basal triangle in **1**. The Au(5)–Au(10) bond is about 15% longer than

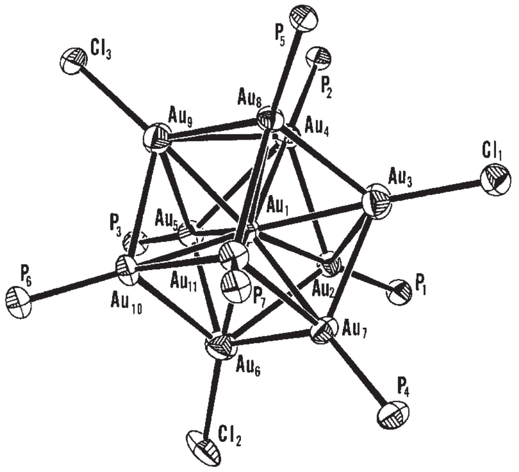

Fig. 1. An ORTEP drawing of **1**. Selected bond-lengths (Å) and angles (°): Au(centered, 1)–Au(apex, 11), 2.6265(6); Au(1)–Au(equatorial, 3, 6, 7, 8, 9, 10), 2.6521(6)–2.7170(7); Au(1)–Au(basal, 2, 4, 5), 2.6628(6)–2.6929(6); Au(11)–Au(eq), 2.8798(7)–3.0227(6); Au(eq)–Au(eq), 2.8264(8)–2.9654(8); Au(bas)–Au(bas), 2.9504(7)–3.0812(7); Au–P, 2.263(3)–2.313(3); Au–Cl, 2.430(3)–2.471(3); Au(11)–Au(1)–Au(3, 6, 7, 8, 9, 10), 65.77(2)–99.84(2); Au(11)–Au(1)–Au(2, 4, 5), 136.04(2)–143.29(2); Au(1)–Au(peripheral)–P, 172.34(8)–178.31(9); Au(1)–Au(peripheral)–Cl, 174.1(1)–177.7(8).

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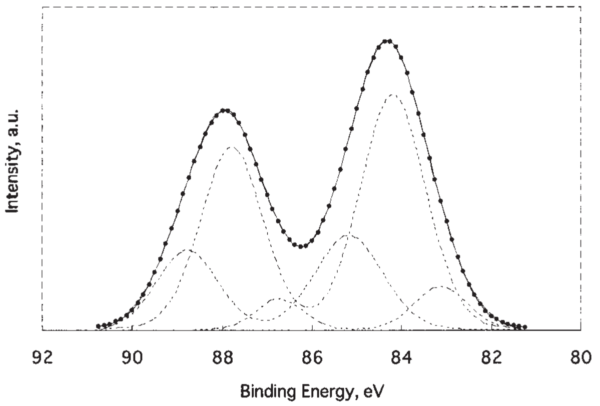

Fig. 2. An XPS spectrum of **1** for $4f$ region of gold atoms. — represents the observed spectrum, ● ● ● ● simulated spectrum, and ······ resolved spectra.

that of metallic gold (2.884 Å). It seems pertinent to note the view by Bellon et al. that the molecular complexity depends upon the crowding of the phosphine ligand around the metal cluster, and the cluster will tend to decrease the size from Au$_{11}$ to Au$_9$ for bulky ligands or increase the size from Au$_{11}$ to Au$_{13}$, provided that suitable ligands are employed.[8a] Perhaps (m-CF$_3$C$_6$H$_4$)$_3$P is the limiting case to form the Au$_{11}$ cluster. A sharp ^{31}P-NMR singlet is detected in a CDCl$_3$ solution ($\delta = 51.0$), which strongly suggests that the distortion of the Au$_{11}$ skeleton is relaxed, and yet **1** is stable in solution. This context is supported by the absorption spectrum of **1** in CH$_2$Cl$_2$($\lambda_{\text{max}} = 296$, 312, and 407 nm), which is quite similar to those of analogous Au$_{11}$X$_3$(PR$_3$)$_7$ clusters.[9]

Figure 2 shows an Au XPS spectrum of **1** for 4f electrons. Two peaks of **1** are distinctly asymmetric, especially the $4f_{7/2}$ peak (ca. 84 eV), which has a weak feature at the lower energy side. Therefore, the curve resolution was made along with the results of single crystal X-ray analysis. In this case, seven peripheral gold atoms bound to the PR$_3$, three peripheral gold atoms bound to Cl, and one central gold atom to give a successful curve-fitting. The binding energy of the core gold atom is 83.1 eV, that of the seven gold atoms is 84.3 eV, and that of the three gold atoms is 85.1 eV. A remarkable result of the fitting is that the binding energy of the core gold atom at the $4f_{7/2}$ level is considerably lower than those of analogous Au$_{11}$X$_3$(PPh$_3$)$_7$ clusters (84.6 eV for X = Cl and 84.5 eV for X = I).[10,11] Another interesting result is that the difference in binding energies between the core gold atom and the three gold atoms bound to Cl is more significant for the present cluster than those for previously reported clusters described above. Perhaps the Au XPS spectrum of **1** reflects a strong distortion from the ideal symmetry caused by introducing CF$_3$ substituents at a *meta*-position of each phenyl ring of PR$_3$ ligands in the solid state.

Experimental

Synthesis. 20 mg (0.5 mmol) of NaBH$_4$ was added to a solution of AuCl{(m-CF$_3$C$_6$H$_4$)$_3$P} (350 mg, 0.5 mmol)[3] in ethanol (50 mL), and the mixture was stirred at room temperature for 4 h. Work-up and recrystallization from CH$_2$Cl$_2$–hexane afford dark-red crystals of **1** (yield 133 mg, 53%). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 51.0 (s) ppm.

X-ray Crystallography. A Bruker SMART-1000/CCD diffract meter with graphite-monochromated Mo Kα radiation; $a = 17.9720(8)$ Å, $b = 27.907(1)$ Å, $c = 32.829(2)$ Å, $\beta = 91.043(1)°$, $V = 16463(1)$ Å^3, $Z = 4$, and $D_{\text{calcd}} = 2.263$ ($P2_1/n$). The reflection data (−60 °C with 2θ range $2.0 \leqq 2\theta \leqq 55°$) were 108099 and 37576 independent reflections with $I \geqq 2\sigma(I)$ were used for refinements. The structural solution and refinements were made as was reported previously.[12b] The final R and R_{w} values are 0.053 and 0.146, respectively, for 2077 parameters. Tables of atomic coordinates, thermal parameters, and bond lengths and angles are available as supporting information (CCDC212441). Selected bond lengths and angles are tabulated in Fig. 1.

XPS Measurements. XPS spectra were obtained on an ULVAC-PHI ESCA-5700MC spectrometer with Mg Kα exciting radiation (1253.6 eV) as was described previously.[12]

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References

1 "Clusters and Colloids," ed by G. Shmid, VCH, Weinheim (1994) and references therein.

2 "Gold," ed by H. Schmidbaur, John Wiley, Chichester (1999) and references therein.

3 K. Nunokawa, S. Onaka, T. Tatematsu, M. Ito, and J. Sakai, *Inorg. Chim. Acta*, **322**, 56 (2001).

4 P. M. V. Calcar, M. M. Olmstead, and A. L. Balch, *J. Chem. Soc., Chem. Commun.*, **1995**, 1773; P. M. V. Calcar, M. M. Olmstead, and A. L. Balch, *Inorg. Chem.*, **36**, 5231 (1997); M. K. Cooper, L. K. Mitcehll, K. Henrick, M. McPartlin, and A. Scott, *Inorg. Chim. Acta*, **84**, L9 (1984).

5 D. T. Hill, G. R. Girard, F. L. McCabe, R. K. Johnson, P. D. Stupik, J. H. Zhang, W. M. Reiff, and D. S. Eggleston, *Inorg. Chem.*, **28**, 3529 (1989); A. Houlton, D. M. P. Mingos, D. M. Murphy, D. J. Williams, L.-T. Phang, and T. S. A. Hor, *J. Chem. Soc., Dalton Trans.*, **1993**, 3629; F. Canales, M. C. Gimeno, P. G. Jones, S. Laguna, and C. Sarroca, *Inorg. Chem.*, **36**, 5206 (1997).

6 S. Onaka, Y. Katsukawa, M. Shiotsuka, O. Kanegawa, and M. Yamashita, *Inorg. Chim. Acta*, **312**, 100 (2001).

7 C. A. Tolman, *Chem. Rev.*, **77**, 3313 (1977).

8 a) P. Belon, M. Manassero, and M. Sansoni, *J. Chem. Soc., Dalton. Trans.*, **1972**, 1481. b) V. G. Albano, P. L. Bellon, M. Manassero, and M. Mansoni, *J. Chem. Soc., Chem. Commun.*, **1970**, 1210.

9 P. A. Barlett, B. Bauer, and S. J. Singer, *J. Am. Chem. Soc.*, **100**, 5085 (1978).

10 R. C. Thiel, R. E. Benfield, R. Zanoni, H. A. Smit, and M. W. Dirken, *Struct. Bonding (Berlin)*, **81**, 1 (1993) and references therein.

11 C. Battistoni, G. Mattogno, R. Zonai, and L. Naldini, *J. Electron Spectrosc. Relat. Phenom.*, **28**, 23 (1982); G. K. Wertheim, J. Kwo, B. K. Teo, and K. A. Keating, *Solid State Commun.*, **55**, 357 (1985); C. Battistoni, G. Mattogno, F. Cariati, L. Naldini, and A. Sgamellotti, *Inorg. Chim. Acta*, **24**, 207 (1977).

12 a) S. Kutsumizu, N. Kojima, and T. Ban, *Chem. Lett.*, **1989**, 345. b) K. Nunokawa, S. Onaka, T. Yamaguchi, M. Yaguchi, T. Tatematsu, S. Watase, M. Nakamoto, and T. Ito, *J. Coord. Chem.*, **55**, 1353 (2002).