# New Gold Clusters $[Au_8L_6](BF_4)_2$ and $[(AuL)_4](BF_4)_2$ ($L = P(mesityl)_3$)[1]

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Recently, we found that the gold oxo complexes $[(AuL)_3O]BF_4$ (L = phosphine) are excellent precursors for the high-yield synthesis of gold clusters.[2] As proposed previously,[3,4] the nature of the cluster produced appears to depend on the steric demands of the ligands. We find that smaller phosphine ligands (L = $PPh_2Me$, $PPhMe_2$) give $[(LAu)_{10}Au]^{3+}$ clusters, while larger phosphine ligands (L = $PPh_3$, $P(p\text{-}ClPh)_3$) give $[(LAu)_6]^{2+}$ clusters.[2b] These results led us to the synthesis of the oxo and hydroxy complexes $[(AuL)_3O]BF_4$ and $[(AuL)_2OH]BF_4$ with the very bulky phosphine ligand L = $P(mesityl)_3$ in efforts to synthesize the unknown trinuclear cluster $(LAu)_3^+$.[5] In this communication, we report the unexpected isolation and structural characterization of a novel gold cluster $(Au_8L_6)^{2+}$ with an unusual open structure. The high-yield preparation of the gold cluster $[(AuL)_4]^{2+}$, a type only recently discovered, is also reported.

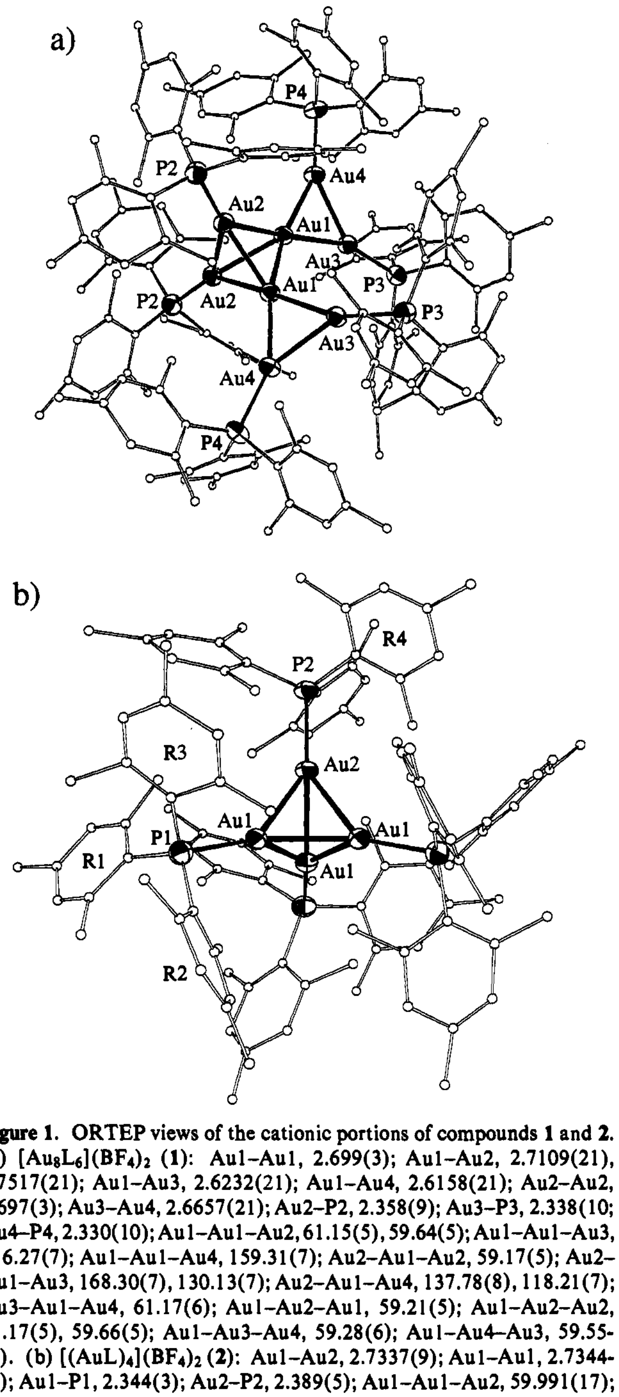

**Figure 1.** ORTEP views of the cationic portions of compounds **1** and **2**. (a) $[Au_8L_6](BF_4)_2$ (**1**): Au1–Au1, 2.699(3); Au1–Au2, 2.7109(21), 2.7517(21); Au1–Au3, 2.6232(21); Au1–Au4, 2.6158(21); Au2–Au2, 2.697(3); Au3–Au4, 2.6657(21); Au2–P2, 2.358(9); Au3–P3, 2.338(10; Au4–P4, 2.330(10); Au1–Au1–Au2, 61.15(5), 59.64(5); Au1–Au1–Au3, 116.27(7); Au1–Au1–Au4, 159.31(7); Au2–Au1–Au2, 59.17(5); Au2–Au1–Au3, 168.30(7), 130.13(7); Au2–Au1–Au4, 137.78(8), 118.21(7); Au3–Au1–Au4, 61.17(6); Au1–Au2–Au1, 59.21(5); Au1–Au2–Au2, 61.17(5), 59.66(5); Au1–Au3–Au4, 59.28(6); Au1–Au4–Au3, 59.55(5). (b) $[(AuL)_4](BF_4)_2$ (**2**): Au1–Au2, 2.7337(9); Au1–Au1, 2.7344(7); Au1–P1, 2.344(3); Au2–P2, 2.389(5); Au1–Au1–Au2, 59.991(17); Au1–Au2–Au1, 60.018(25); Au1–Au1–P1, 144.28(9), 146.99(9); Au2–Au1–P1, 142.84(9). Arbitrary spheres for C, 50% probability ellipsoids for Au and P. Atoms with the same name are related by a 2-fold (**1**) or a 3-fold (**2**) axis.

The oxo complex $[(AuL)_3O]BF_4$ (L = $P(mesityl)_3$) (**3**)[6] is prepared similarly to previously reported Au oxo complexes (eq 1).[7] An alternate synthetic procedure (eq 2), also used previously

$$\mathrm{LAuCl + Ag_2O + NaBF_4 \rightarrow \underset{\mathbf{3}}{[(LAu)_3O]BF_4} + AgCl + \cdots} \tag{1}$$

$$\mathrm{LAuCl + AgBF_4 + NaOH \rightarrow \underset{\mathbf{4}}{[(LAu)_2OH]BF_4} + AgCl + \cdots} \tag{2}$$

for the preparation of Au oxo complexes, unexpectedly gives the hydroxo complex **4**[8] and not **3**.[9] Both **3** and **4** react with excess CO (3 atm) in THF to give two new Au clusters (eq 3). Carbon

$$\mathrm{\underset{\mathbf{3}}{[(LAu)_3O]BF_4} \text{ or } \underset{\mathbf{4}}{[(LAu)_2OH]BF_4} \xrightarrow{CO} \underset{\mathbf{1}}{[Au_8L_6](BF_4)_2} + \underset{\mathbf{2}}{[(AuL)_4](BF_4)_2} + L + \cdots} \tag{3}$$

monoxide addition to homogeneous, colorless THF solutions of oxo complex 3 rapidly (<1 h) gives mixtures of $[Au_8L_6](BF_4)_2$ (**1**)[10] and $[(AuL)_4](BF_4)_2$ (**2**)[11] in about a 3:2 ratio along with free L ($^{31}$P NMR). Yellow crystals of **1** form from the filtered reduced solutions after several days at –30 °C. The structure of **1**[12] shows a $Au_4$ tetrahedral core with LAu–AuL fragments side-

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[1] Late Transition Metal Oxo and Imido Complexes. 13. Part 12: Li, J. J.; Sharp, P. R. *Inorg. Chem.* **1994**, *33*, 183–184.

[2] (a) Ramamoorthy, V.; Wu, Z.; Yang, Y.; Sharp, P. R. *J. Am. Chem. Soc.* **1992**, *114*, 1526–1527. (b) Sharp, P. R.; Yang, Y.; Wu, Z.; Ramamoorthy, V. In *The Chemistry of the Copper and Zinc Triads*; Welch, A. J., Chapman, S. K., Eds.; The Royal Society of Chemistry: Cambridge, U.K., 1993.

[3] Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237–324.

[4] Steggerda, J. J. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 164.

[5] Two and three atom gold clusters have been mentioned or communicated, but full details of their synthesis and characterization have never appeared: Mingos, D. M. P. *Pure Appl. Chem.* **1980**, *52*, 705–712. Kanter, H.; Dimroth, K. *Tetrahedron Lett.* **1975**, *8*, 545–546.

[6] Data for **3**: $^1$H NMR ($CD_2Cl_2$) $\delta$ 6.83 (br s, 2H, Ph), 2.41 (br s, 3H, $CH_3$), 2.31 (br s, 3H, $CH_3$), 1.74 (br s, 3H, $CH_3$); $^{31}$P NMR (122 MHz, $CH_2Cl_2$, external $H_3PO_4$ ref) $\delta$ –13.4. Anal. Calcd (Found) for $C_{81}H_{99}Au_3BF_4OP_3$: C, 52.33 (51.46); H, 5.37 (5.24).

[7] These procedures follow those used for the L = $PPh_3$ oxo complex (Nesmeyanov, A. V.; Perevalova, E. G.; Struchkov, Y. T.; Antipin, M. Y.; Grandberg, K. I.; Dyadchenko, V. P. *J. Organomet. Chem.* **1980**, *201*, 343–349) and as further developed for other phosphines (Yang, Y.; Ramamoorthy, V.; Sharp, P. R. *Inorg. Chem.* **1993**, *32*, 1946–1950).

[8] Data for (**4**): $^1$H NMR ($CD_2Cl_2$) $\delta$ 6.93 (br s, 2H, Ph), 6.60 (br s, 1H, OH), 2.36 (br s, 3H, $CH_3$), 2.24 (br s, 3H, $CH_3$), 1.77 (br s, 3H, $CH_3$); $^{31}$P NMR (122 MHz, $CH_2Cl_2$, external $H_3PO_4$ ref) $\delta$ –18.2. Anal. Calcd (Found) for $C_{54}H_{67}Au_2BF_4OP_2$: C, 50.71 (50.87); H, 5.27 (5.27).

[9] Schmidbaur et al. have also reported the preparation of oxo complex **3**: Kolb, A.; Bissinger, P.; Schmidbaur, H. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1580. However, the reported spectroscopic and analytical data match those of our hydroxo complex **4**.

[10] Data for **1**: $^1$H NMR (500 MHz, $CD_2Cl_2$) $\delta$ 6.8 (br, $\nu_{1/2}$ = 104 Hz, 2H, Ph), 2.25 (br, $\nu_{1/2}$ = 225 Hz, 6H, $CH_3$), 1.65 (br, $\nu_{1/2}$ = 138 Hz, 3H, $CH_3$); $^{31}$P NMR (122 MHz, $CH_2Cl_2$, external $H_3PO_4$ ref) $\delta$ 29.6 (d, $J$ = 54 Hz), 25.9 (d), 23.21 (s). At low temperatures, the $^1$H NMR spectra sharpen but are very complex, presumably due to the presence of rotamers.

[11] Data for **2**: $^{31}$P NMR (122 MHz, $CH_2Cl_2$, external $H_3PO_4$ ref) $\delta$ 24.36 (q, $J_{PP}$ = 29.8 Hz), 21.80 (d). The $^1$H NMR (500 MHz, $CD_2Cl_2$) spectra are complex, presumably due to the presence of rotamers. Major peaks ($\delta$): 7.05, 6.91, 6.81 (Ph); 2.49, 2.46, 2.36, 2.20, 1.98, 1.96, 1.75, 1.71, 1.57 (Me).

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bonded to two of the core Au atoms and phosphines bonded to the remaining two core Au atoms (Figure 1a). This results in two Au atoms (Au1) bonded to only five Au atoms and no ligands. Such an open, apparently unsaturated structure is unique in Au cluster chemistry. Four other Au clusters based on a tetrahedral core, $[Au_4I_2(PPh_3)_4]$, $[Au_4I_2(dppm)_3]$, $[Au_5(dppm)_3(dppm\text{-}H)]^{2+}$, and $[Au_6(dppp)_4]^{2+}$, have been reported but have one or more P atoms coordinated to each Au center.[13]

Complex **2** is best prepared from the CO reaction of the hydroxo complex **4**. Stirring a THF suspension of **4** for 6 h under 3 atm of CO gives a white solid, which upon recrystallization from $CH_2Cl_2$/pentane affords $[(AuL)_4](BF_4)_2$ (**2**) in 80% yield. Some **1** is also detected ($^{31}P$ NMR) in the THF filtrate. The structure of **2**[14] shows a tetrahedral cluster residing on a 3-fold axis (Figure 1b). The bond distance between the three equivalent Au atoms Au1 is 2.7344(7) Å, and that to unique Au atom Au2 is essentially identical, at 3.7337(9) Å. Recently, Schmidbaur and co-workers[15] isolated (5% yield) and structurally characterized the $PBu^t_3$ analog of cluster **2**. The Au–Au distances in the $PBu^t_3$ analog are slightly shorter (2.7031(9)–2.7302(7) Å), perhaps as a result of reduced crowding with the smaller $PBu^t_3$. Consistent with this is the observation that the $^{31}P$ NMR spectra of **2** show two different types of phosphines (as in the solid), apparently as a result of the "cogging" of the mesityl groups.

We have just begun to explore the chemistry of these new gold clusters. Complex **1** is particularly interesting for its low Au-to-phosphine ratio and its very open structure, suggesting a high degree of unsaturation. Indeed, treatment of **1** with $PPh_3$ collapses the open structure, giving known $[(AuPPh_3)_8](BF_4)_2$.[16]

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**Note Added in Proof**: Cluster **1** may be considered a "cluster-of-clusters" (Teo, B. K.; Zhang, H. *J. Cluster Science* **1990**, *1*, 155–187) formed by the vertex fusion of tetrahedral cluster **2** with two triangular $(LAu)_3$ clusters.

**Supplementary Material Available**: Structural reports for **1** and **2**, including tables of atom parameters and bond distances and angles (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(12) Crystals of **1**·$(THF)_x$ from THF are monoclinic, $C2/n$, with $a = 36.577(11)$ Å, $b = 31.178(4)$ Å, $c = 20.581(5)$ Å, $\beta = 118.390(10)°$, $V = 20648(8)$ Å$^3$, $Z = 4$, $d_{calc} = 1.35$ g/cm$^3$, $\mu$(Mo K$\alpha$) = 4.31 mm$^{-1}$, CAD4 diffractometer, $T = 22$ °C, 9608 reflections, 5731 observed ($>2\sigma$), H atoms not included, $R/R_w = 0.064/0.094$.

(13) Demartin, F.; Manassero, M.; Naldini, L.; Ruggeri, R.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1981**, 22. van der Velden, J. W. A.; Bour, J. J.; Pet, R.; Bosman, W. P.; Noordik, J. H. *Inorg. Chem.* **1983**, *22*, 3112. van der Velden, J. W. A.; Vollenbroek, F. A.; Bour, J. J.; Beurskens, P. T.; Smits, J. M. M.; Bosman, W. P. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 148. van der Velden, J. W. A.; Bour, J. J.; Steggerda, J. J.; Beurskens, P. T.; Roseboom, M.; Noordik, J. H. *Inorg. Chem.* **1982**, *21*, 4321.

(14) Crystals of **2**·$(CH_2Cl_2)_3$ from $CH_2Cl_2$/pentane are trigonal, $P31c$, with $a = 16.286(1)$ Å, $c = 25.894(5)$ Å, $V = 5948(1)$ Å$^3$, $Z = 2$, $d_{calc} = 1.55$ g/cm$^3$, $\mu$(Cu K$\alpha$) = 10.12 mm$^{-1}$; CAD4 diffractometer, $T = 22$ °C, 3024 reflections, 2773 observed ($>2.5\sigma$), $R/R_w = 0.034/0.043$.

(15) Zeller, E.; Beruda, H.; Schmidbaur, H. *Inorg. Chem.* **1993**, *32*, 3203–3204.

(16) Manassero, M.; Naldini, L.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1979**, 385. Vollenbroek, F. A.; Bosman, W. P.; Bour, J. J.; Noordik, J. H.; Beurskens, P. T. *J. Chem. Soc., Chem. Commun.* **1979**, 387.