readily transformed, allowing for the preparation of additional ferrocene derivatives containing four-carbon heteroannular bridges. Further studies of this novel cyclization reaction of 1,1′-bis((trimethyl)ethynyl)ferrocene and similar systems are currently in progress.

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Synthesis and X-ray Characterization of the Neutral Organometallic Gold Cluster $[Au_{10}(C_6F_5)_4(PPh_3)_5]$

Antonio Laguna,* Mariano Laguna, and M. Concepción Gimeno

Departamento de Química Inorgânica, Instituto de Ciencia de Materiales de Aragôn,
Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Peter G. Jones

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30,
W-3300 Braunschweig, Germany

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Summary: The reaction of $[Au_9(PPh_3)_8](NO_3)_3$ with 3 equiv of $NBu_4[Au(C_6F_5)_2]$ affords the neutral cluster $[Au_{10}(C_6F_5)_4(PPh_3)_5]$ in high yield. X-ray diffraction reveals that the cluster has a toroidal geometry based on a ring of edge- and face-sharing tetrahedra that share a common central vertex. It crystallizes in space group $P2_1/c$ with a = 18.339 (4) Å, b = 15.603 (4) Å, c = 41.510 (12) Å, β = 95.10 (2)°, and Z = 4. This cluster represents the second example of both an Au_{10} and an organometallic gold cluster.

Gold forms a wide range of cluster compounds in which the metal has an oxidation state between 0 and +1. These compounds are generally stabilized by tertiary phosphine ligands,[1,2] in contrast to many high-nuclearity metal clusters that have CO as ligands.[2,3]

Many examples of gold clusters are known from Au_3 to Au_{13} with a variety of geometries and have been classified by Mingos and Hall[2] as (a) spherical polyhedral clusters characterized by a total of $12n + 18$ valence electrons (n is the number of peripheral gold atoms), e.g. $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$,[4] and (b) toroidal or elliptical polyhedral clusters characterized by a total of $12n + 16$ valence electrons, e.g. $[Au_9\{P(p\text{-tol})_3\}_8]^{3+}$.[5]

The lack of organometallic gold clusters in this field is noteworthy; only one example has been reported, namely $[Au_5(dppmH)_3(dppm)](NO_3)_2$,[6,7] where one deprotonated dppm ligand forms an Au–C bond. Similarly, Au_{10} derivatives are very poorly represented; only the cluster $[Au_{10}Cl_3(PCy_2Ph)_6](NO_3)$[8] has been synthesized in low yield.

Here we report the synthesis and characterization by elemental analysis, IR and NMR spectroscopy, fast atom bombardment mass spectrometry, and single-crystal X-ray diffraction of $[Au_{10}(C_6F_5)_4(PPh_3)_5]$.

The reaction of $[Au_9(PPh_3)_8](NO_3)_3$ with $NBu_4[Au(C_6F_5)_2]$ (molar ratio 1:3) in dichloromethane yielded, after separation of NBu_4NO_3, the orange solid $[Au_{10}(C_6F_5)_4(PPh_3)_5]$ (80% yield).[9] The fact that no other cluster species has been detected and that $[Au(C_6F_5)PPh_3]$ is also formed led us to propose the reaction

$$[Au_9(PPh_3)_8](NO_3)_3 + 3NBu_4[Au(C_6F_5)_2] \rightarrow [Au_{10}(C_6F_5)_4(PPh_3)_5] + 3NBu_4NO_3 + 2[Au(C_6F_5)PPh_3] + PPh_3$$

The IR spectrum of $[Au_{10}(C_6F_5)_4(PPh_3)_5]$ exhibits bands due to the C_6F_5 group[10,11] at 1496 (s), 1068 (s, br), 951 (s), and 782 (s) cm^{-1}; the last band is very sensitive to the nature of the ligand in the trans position and to the oxidation state and therefore appears for $[Au(C_6F_5)_2]^-$ at 780 cm^{-1} and for $[Au(C_6F_5)L]$ complexes in the range 790–800 cm^{-1}. In our complex this band is found between these two values.

The mass spectrum (over m/z 2000) gave the most abundant mass ion at m/z 3782, which corresponds not

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(9) Procedure: To a dichloromethane solution (30 mL) of $[Au_9(PPh_3)_8](NO_3)_3$ (0.405 g, 0.1 mmol) was added $NBu_4[Au(C_6F_5)_2]$ (0.232 g, 0.3 mmol). After 3 h the solvent was evaporated to dryness and 30 mL of diethyl ether added. The white solid (NBu_4NO_3) was filtered off and the solution evaporated to ca. 10 mL. Addition of n-hexane gave $[Au_{10}(C_6F_5)_4(PPh_3)_5]$ (80%). Anal. Calcd: C, 34.67; H, 1.91. Found: C, 34.67; H, 1.86. $\Lambda_M = 5\ \Omega^{-1}\ cm^2\ mol^{-1}$ in acetone. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 58.5 (s, br) ppm; −60° C, δ 64.4 (br), 53.3 (br), 49.4 (br) ppm. ^{19}F NMR ($CDCl_3$): δ −112.51 (m, 4 F, o-F) −162.79 [t, 2 F, p-F, J(FF) = 20.8 Hz], −163.36 (m, 4 F, m-F).

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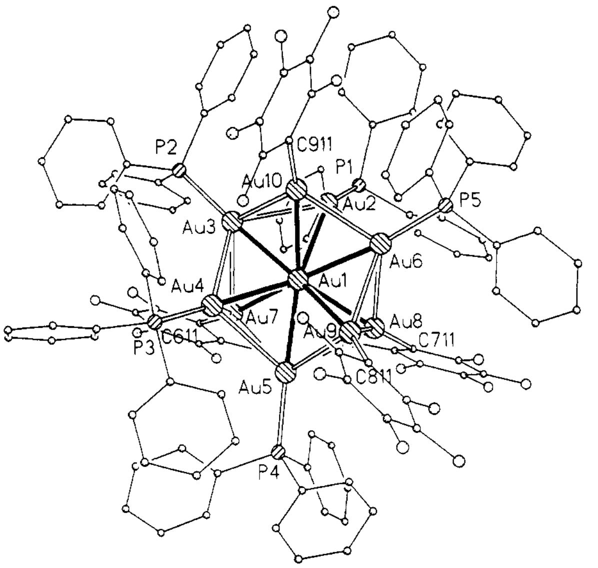

Figure 1. Molecular structure of $[Au_{10}(C_6F_5)_4(PPh_3)_5]$ (Au, P, and ipso C atoms of C_6F_5 are labeled). Selected bond lengths (Å): Au1–Au3 = 2.653 (3), Au1–Au5 = 2.651 (3), Au1–Au7 = 2.786 (3), Au1–Au9 = 2.754 (3), Au1–Au2 = 2.711 (2), Au1–Au4 = 2.691 (2), Au1–Au6 = 2.671 (2), Au1–Au8 = 2.724 (3), Au1–Au10 = 2.776 (3). Au–C bond lengths lie in the range 2.05–2.11 (3) Å and Au–P in the range 2.26–2.28 (1) Å.

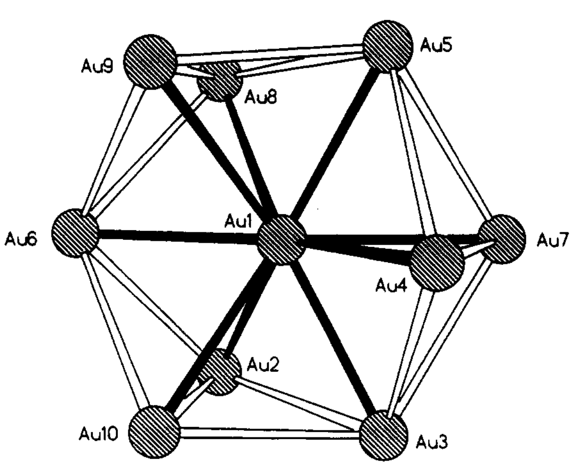

Figure 2. Skeletal geometry of the cluster $[Au_{10}(C_6F_5)_4(PPh_3)_5]$.

to the molecular ion $[Au_{10}(C_6F_5)_4(PPh_3)_5]^+$ ($[M]^+$) but to $[M - C_6F_5]^+$. Other fragmentation peaks have been assigned.[12]

$^{31}P\{^1H\}$ NMR spectroscopy does not provide much information since only one resonance at 58.5 (br) ppm is observed at room temperature. Variable-temperature spectra reveal three broad resonances at 66.4, 53.3, and 49.4 ppm in the ratio 2:1:2, but no *J*(PP) coupling constants are observed, probably due to rapid intramolecular skeletal rearrangements which are a common feature in gold cluster chemistry. The ^{19}F NMR spectrum shows three signals characteristic of equivalent C_6F_5 groups;[9] the spectrum was also measured at variable temperature, but at –60 °C only broadening of the signals was observed.

Crystals of the complex (as a dichloromethane disolvate) suitable for X-ray studies were obtained from dichloromethane/petroleum ether as orange plates.[13] The structure is shown in Figure 1, with selected bond lengths and angles. Figure 2 shows the skeletal geometry, which is related to that of $[Au_{10}Cl_3(PCy_2Ph)_6](NO_3)$, which also contains a hexagonal ring of six edge- and face-sharing $AuAu_3L_3$ tetrahedra with a common central atom. This geometry for the cluster is consistent with its polyhedral electron count of 124, i.e. 12*n* + 16.[14,15]

In contrast to the case for $[Au_{10}Cl_3(PCy_2Ph)_6](NO_3)$, where the higher connectivity sites were occupied by the less sterically demanding chlorine ligands, in $[Au_{10}(C_6F_5)_4(PPh_3)_5]$ these gold atoms are joined to PPh_3. The other ligands are located around the cluster core in such a way that the symmetry is approximately C_{2v}. The Au–Au distances involving the central gold atom fall in the range of 2.651 (3)–2.786 (3) Å and are shorter than most of the peripheral Au–Au distances (2.695 (2)–2.970 (2) Å). The short peripheral bonds are those of the gold atoms situated in the face-sharing tetrahedra: Au4–Au7 = 2.695 (2), Au2–Au10 = 2.702 (2), and Au8–Au9 = 2.711 (2) Å. This contrasts with the usual observation in high-nuclearity centered clusters, where the radial Au–Au bonding interactions are more important.

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Supplementary Material Available: A description of the crystal structure determination, including tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, and thermal parameters (11 pages). Ordering information is given on any current masthead page.

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[12] Mass spectrum (*m*/*z*): 3781.7 $[M - C_6F_5]^+$ (100%); 3164.9 $[M - 2C_6F_5]^+$ (20%); 3417.9 $[M - 2C_6F_5 - Au]^+$ (48%); 3154.7 $[M - C_6F_5 - Au(C_6F_5)PPh_3]^+$ (61%); 2529.1 $[M - C_6F_5 - 2Au(C_6F_5)PPh_3]^+$ (43%).

[13] Crystal data: $C_{116}H_{79}Au_{10}Cl_4F_{20}P_5$, M_r = 4119.1, monoclinic, space group $P2_1/c$, a = 18.339 (4) Å, b = 15.603 (4) Å, c = 41.510 (12) Å, β = 95.10 (2)°, V = 11831 (5) Å^3, Z = 4, D_x = 2.131 Mg m^{-3}, $F(000)$ = 7552, μ(Mo Kα) = 12.6 mm^{-1}, T = –95 °C. A total of 16 737 intensities were measured on a Siemens R3 diffractometer with an LT-2 low-temperature attachment to $2\theta_{max}$ = 45°. The structure was solved by direct methods and extended by difference syntheses. Refinement proceeded to R = 0.075 for 6992 unique observed reflections (Au, P anisotropic; C, F, Cl isotropic).

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