COMMUNICATION

Dalton
www.rsc.org/dalton

A step forward in gold–silver metallophilicity. An $AuAg_4$ moiety with a square pyramidal arrangement†

Eduardo J. Fernández,*[a] Antonio Laguna,*[b] José M. López-de-Luzuriaga,[a] Miguel Monge,[a] Manuel Montiel,[a] M. Elena Olmos,[a] Javier Pérez,[a] Raquel C. Puelles[a] and Juan C. Sáenz[a]

[a] *Departamento de Química, Universidad de La Rioja, Grupo de Síntesis Química de La Rioja, UA-CSIC. Complejo Científico-Tecnológico, 26004, Logroño, Spain. E-mail: eduardo.fernandez@dq.unirioja.es*

[b] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009, Zaragoza, Spain. E-mail: alaguna@posta.unizar.es; Fax: +34 976 761187; Tel: +34 976 761185*

Received 3rd December 2004, Accepted 23rd February 2005
First published as an Advance Article on the web 7th March 2005

DOI: 10.1039/b502701m

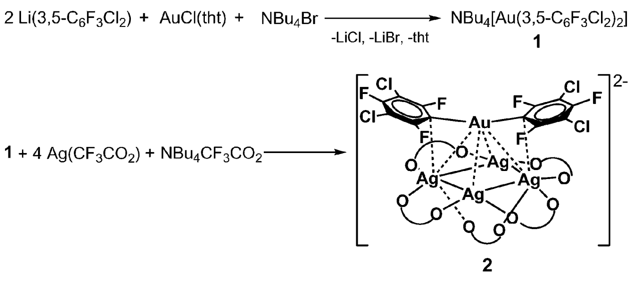
By reaction of the Lewis base $NBu_4[Au(3,5\text{-}C_6F_3Cl_2)_2]$ and $AgCF_3COO$ in the presence of NBu_4CF_3COO the heterometallic compound $(NBu_4)_2[Au(3,5\text{-}C_6F_3Cl_2)_2Ag_4(CF_3COO)_5]$ (2) is obtained. The structure displays an unprecendented square pyramidal $AuAg_4$ arrangement built up through four Au···Ag closed-shell interactions and two Au–C–Ag 3c–2e⁻ bridges.

Among nonbonding interactions between closed-shell metals, the most studied are the aurophilic Au(I)–Au(I) interactions.[1] However, there is a growing interest in mixed-metal interactions[2] and, thus, among them, a number of complexes containing argento–aurophilic contacts have been reported recently.[3] The most common strategy for the synthesis of heteronuclear Au^I/Ag^I systems is the use of asymmetric polydentate ligands that can act as a bridge between the metal centres,[3,4] and, in particular, the reaction of $[Au(L\text{–}L')_2]^+$ with equimolecular amounts of a silver(I) salt, such as AgTfO ($TfO = CF_3SO_3$),[3b,4b] $Ag(OClO_3)$,[4a] or $AgBF_4$.[3d] A different synthetic strategy consists of the reaction between a donor metallic system, such as $[Au(C_6F_5)_2]^-$,[5] $[Au(CH_2PR_3)_2]^+$,[6] $[Au_2(CH_2SiMe_3)_2(\mu\text{-dppm})]$[7] or $[Au(\mu\text{-}C^2,N^3\text{-bzim})]_3$[8] (bzim = 1-benzylimidazolate), and the same acid Ag^+ salts as above. However, although the complexes obtained through these or alternative procedures present a variety of structural dispositions, they always contain an acidic silver(I) centre surrounded by a number of gold(I) atoms that goes from a minimum of one[3–6,9] to a maximum of six,[8,10] which means that each acidic silver atom needs at least one donor fragment to form an stable system.

On the other hand, as has been reported by Schmidbaur,[3e] while in (phosphine)gold(I) perfluorocarboxylates the metals are always linearly two-coordinate with monohapto carboxylate groups, in the corresponding (phosphine)silver(I) perfluorocarboxylates the coordination number of the metal atoms can be expanded with the carboxylate groups forming O,O′-dihapto bridges between the metal atoms. Donor-free silver(I) perfluorocarboxylates are known to form cyclic dimers of the type $[Ag(\mu\text{-}O,O'\text{-}OC(O)CR_F)]_2$ in the solid state. This dimeric unit is also retained as a core with a planar eight-membered ring in the tetranuclear complexes $[(C_6F_5)Au(\mu\text{-}PPh_2CH_2SPh)Ag(\mu\text{-}CF_3CO_2)]_2$,[4b] or $[\{(4\text{-}Me_2NC_6H_4)Ph_2P\}Au(\mu\text{-}C_2F_5CO_2)Ag(\mu\text{-}C_2F_5CO_2)]_2$,[3e] both of them showing Au···Ag contacts in addition to the Ag···Ag interactions present in the dimeric core. Nevertheless, as before, the ratio between gold and silver is still one.

Taking into account these two facts, we wondered if the reaction of a basic $[AuR_2]^-$ (R = perhalophenyl group) anion with silver(I) trifluoroacetate in different molar ratios could lead to the synthesis of heteronuclear compounds in which a unique bis(perhalophenyl)aurate(I) unit could maintain Au···Ag metallophilic interactions with more than one silver atom. In this regard, the capability of C_6F_5 and $3,5\text{-}C_6F_3Cl_2$ to act as bridging groups in certain intermediates in catalytic processes that involve heterometallic Pd/Au systems,[11] prompted us to use the corresponding bis(aryl)aurates(I) as bases in order to facilitate the formation of Au···Ag interactions taking advantage of both, the donor characteristics and the bridging capabilities of these groups.

Although the complex $[Au(C_6F_5)_2]^-$ has been known since 1976,[12] the $3,5\text{-}C_6F_3Cl_2$ precursor has not yet been described. By reaction of a freshly prepared solution of $Li(3,5\text{-}C_6F_3Cl_2)$ in Et_2O and at −78 °C with [AuCl(tht)] and further addition of NBu_4Br (2 : 1 : 1) the new anionic homoleptic complex $NBu_4[Au(3,5\text{-}C_6F_3Cl_2)_2]$ (**1**) was isolated as a white solid with analytical and spectroscopic properties in agreement with the proposed stoichiometry (Scheme 1). Its IR spectrum shows very strong bands at 1587, 1562, 1047 and 775 cm⁻¹, due to the aryl groups bonded to gold(I) and a strong band at 883 cm⁻¹, corresponding to the cation. In its ^{19}F NMR spectrum two signals located at −89.1 and −119.1 ppm with relative intensities 2 : 1, due to the *ortho* and *para* fluorine atoms, are observed. Finally, its mass spectrum (ES⁻) shows a unique peak at *m*/*z* 597, corresponding to the anion $[Au(3,5\text{-}C_6F_3Cl_2)_2]^-$.†



Scheme 1 Synthesis of complexes **1** and **2**.

Further reactions of $NBu_4[AuR_2]$ with $Ag(CF_3CO_2)$ produces different results depending on the aryl group and, thus, the pentafluorophenyl derivative leads to oily mixtures that could not be characterized whatever the molar ratio. In contrast, when complex **1** is treated with equimolecular amounts of silver(I) trifluoroacetate a yellow solid of stoichiometry $(NBu_4)_2[Au(3,5\text{-}C_6F_3Cl_2)_2Ag_4(CF_3CO_2)_5]$ (**2**) was obtained in a moderate yield together with a mixture of unreacted $NBu_4[Au(3,5\text{-}C_6F_3Cl_2)_2]$ and Ag^0 (Scheme 1). Complex **2** can also be obtained as a pure product and in a higher yield when the same reaction is carried

---

† Electronic supplementary information (ESI) available: Experimental section. See http://www.rsc.org/suppdata/dt/b5/b502701m/

out in a 1 : 4 molar ratio of metal precursors with addition of one equivalent of NBu_4CF_3COO.†

By layering a dichloromethane solution of **2** with *n*-hexane, single crystals suitable for its X-ray diffraction study were obtained.‡ The anion $[Au(3,5\text{-}C_6F_3Cl_2)_2Ag_4(\mu\text{-}CF_3CO_2)_5]^{2-}$ (Fig. 1) contains an unexpected and unprecedented pentanuclear $AuAg_4$ core with the silver atoms forming the base of a square pyramid and the gold centre in the apical position. The aryl groups are bonded to the gold atom (which adopts a slightly distorted linear environment) and also interact with two silver centres, thus acting as asymmetric bridging ligands, while the trifluoroacetates bridge each two Ag(I) atoms. Four of these $CF_3CO_2^-$ anions are nearly parallel to the plane formed by the silver atoms, while the fifth trifluoroacetate forms an angle of 60° with the same plane. The former bind the silver atoms with Ag–O bond distances in the range 2.237–2.335 Å, while the latter shows, in addition to two Ag–O bond distances of 2.349(6) and 2.441(6) Å, two Ag···O weak interactions of 2.546(6) and 2.699(7) Å (see Fig. 1). The Ag–Ag distances, in the range 2.8424(8)–2.9396(7) Å, are similar to those found in other perfluorocarboxylates complexes containing $CF_3CO_2^-$ [4b] (2.8155(9) Å) or $C_2F_5CO_2^-$ [3e] (2.9439(6) Å) anions bridging two silver atoms. The Au–Ag distances (between 2.9019(6) and 3.0134(6) Å) are comparable to those observed in the phenylacetylide clusters $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$[9a] (2.989(1)–3.028(1) Å) or $[Au_3Ag_2(C_2Ph)_6]^-$ [13] (2.876(4)–3.096(5) Å) or to those found in the dinuclear species $[AuAg(Ph_2PCH_2SPh)_2](TfO)_2$[4b] (2.9314(5) Å), $[AuAg(2\text{-}Ph_2PC_6H_4NH_2)_2](TfO)_2$[3b] (2.9931(12) Å), $[AuAg(MTP)_2]$ (MTP = diphenylmethylenethiophosphinate)[3a] (2.9124(13) Å), all of them containing bridging ligands between the Au^I and Ag^I, while in **2** only two of these interactions are supported by the aryl bridging ligands. These aryl groups are asymmetrically bonded to the metals, showing Au–C distances of 2.067(7) and 2.068(7) Å and Ag–C distances of 2.450(6) and 2.439(6) Å.

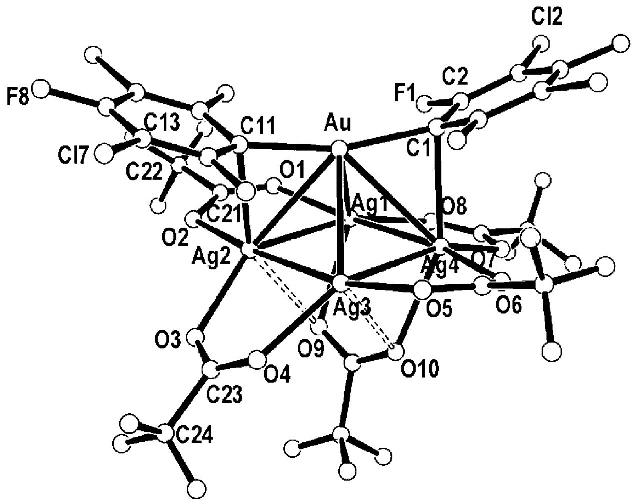


Fig. 1 Crystal structure of the cation of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angle (°): Au–Ag(1) 3.0134(6), Au–Ag(2) 2.9019(6), Au–Ag(3) 2.9364(6), Au–Ag(4) 2.9421(6), Ag(1)–Ag(2) 2.8424(8), Ag(1)–Ag(4) 2.8563(7), Ag(2)–Ag(3) 2.9396(7), Ag(3)–Ag(4) 2.8652(8), Au–C(1) 2.067(7), Au–C(11) 2.068(7), Ag(4)–C(1) 2.450(6), Ag(2)–C(11) 2.439(6), Ag(1)–O(1) 2.272(5), Ag(1)–O(8) 2.257(5), Ag(1)–O(9) 2.441(6), Ag(2)–O(2) 2.335(5), Ag(2)–O(3) 2.237(6), Ag(3)–O(4) 2.251(6), Ag(3)–O(5) 2.255(5), Ag(4)–O(6) 2.330(5), Ag(4)–O(7) 2.297(6), Ag(4)–O(10) 2.349(6), Ag(2)–O(9) 2.546(6), Ag(3)–O(10) 2.699(7); C(1)–Au–C(11) 164.4(2).

In its IR spectrum, this complex shows bands due to the aryl groups bonded to gold(I) (1558, 1557, 1057 and 794 cm⁻¹), to the tetrabutyl ammonium cation (887 cm⁻¹) and to the trifluoroacetate anions (1652 and 1210 cm⁻¹), shifted from those due to the metallic precursor complexes. The resonances due to the fluorine atoms of the CF_3COO^- and $3,5\text{-}C_6F_3Cl_2$ groups are observed in its ^{19}F NMR spectrum at −73.0 (s) (CF_3COO), −83.4 (m) (F_o) and −109.5 (m) (F_p) ppm, whose relative integration is in accordance with the proposed stoichiometry (15 : 4 : 2) (Fig. 2). Interestingly, the resonances due to the aryl groups are significantly shifted to downfield from those found for the starting gold precursor, 6 ppm for the *ortho* signal or 10 ppm for the *para* one, indicating a different magnetic environment that could be related to the interaction between the basic $[Au(C_6F_3Cl_2)]^-$ group and the acid silver atoms that remain in solution. In fact, it has been reported that the resonances due to the *ortho*- and *para*-fluorine atoms of bridging C_6F_5 or $C_6F_3H_2$ groups appear at lower fields than those corresponding to terminal ones.[14] It is worth noting that the permanence of such M···M′ interactions in solution is not common, although they seem to be kept in this particular case, which makes this complex more attractive. Variable-temperature ^{19}F NMR study of complex **2** in $CDCl_3$ reveals some interesting features. Thus, at room temperature (293 K) exchange broadening is already observed for all peaks, consistent with the existence of a dynamic behaviour in solution. Looking at the signal corresponding to the $CF_3CO_2^-$ anion at δ −73.0 ppm (293 K) an increasing line-width broadening is observed on decreasing the temperature. At 223 K the signal splits into two broad peaks at δ −72.6 and −73.5 ppm and a third sharp peak at δ −71.9 ppm. This situation would represent the $CF_3CO_2^-$ ligands in different coordination environments.[15] Thus, the two broad peaks may correspond to the two types of trifluoroacetate ligands bridging the Ag(I) centres in the pyramid base in which the CF_3 groups can be oriented close to the $[Au(C_6F_3Cl_2)_2]^-$ unit or away from it (see the X-ray structure in Fig. 1). On the other hand, the sharp peak could correspond to the fifth trifluoroacetate ligand placed below the pyramid base and bonded to four silver atoms that could be in a more fixed fashion, since it might not participate in two different conformations as the other four trifluoroacetate ligands at that temperature.

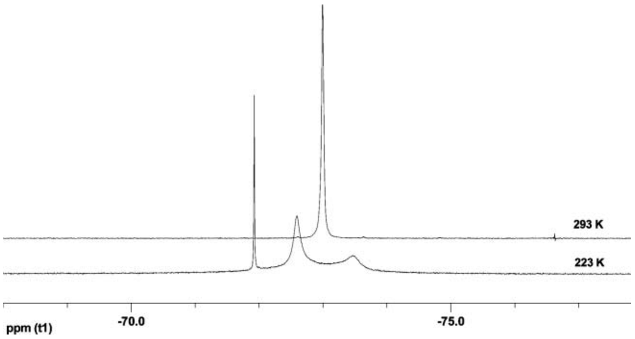


Fig. 2 ^{19}F NMR spectra at 293 and 223 K of complex **2**. The region displayed corresponds to the $CF_3CO_2^-$ ligands.

Also, the conductivity measurement of this complex in dilute acetone solutions gives a value of 208 ohm⁻¹ cm² mol⁻¹, characteristic of 1 : 2 electrolytes. This value contrasts with those of 92 and 10 ohm⁻¹ cm² mol⁻¹ observed for the starting materials **1** and $AgCF_3CO_2$, which are in accordance with a 1 : 1 electrolyte and with a non-conducting species, respectively. This results seem to indicate that the pentanuclear anion $[Au(3,5\text{-}C_6F_3Cl_2)_2Ag_4(\mu\text{-}CF_3CO_2)_5]^{2-}$ remains in solution probably due to the stability that the presence of the intermetallic interactions and the perhalophenyl and trifuoroacetate bridging ligands confers to the molecule.

On the other hand, and in contrast to what was observed in other Au/Ag complexes previously reported that in addition display Au···Au interactions,[3d,5c] the lack of such contacts in the case of complex **2** seems to be the responsible for its non-luminescent behaviour in the solid state both at room temperature and at 77 K. In degassed chloroform solution complex **2** displays a weak emission at 381 nm (exc. 330 nm) appearing at fairly similar energy (350 nm) than the precursor gold complex $NBu_4[Au(3,5\text{-}C_6F_3Cl_2)_2]$. This fact as well as the high energy values found, allows us to assign this emission to arise from π–π* transitions in the perhalophenyl rings.

Ab initio calculations are currently in progress in order to study the nature of both the metallophillic interactions and the 2c–3e⁻ bridges responsible for this unusual $Au \cdots Ag_4$ arrangement.

The D.G.I. (MEC)/FEDER (CTQ2004-05495) project is acknowledged for financial support. M. Monge thanks the MEC-Universidad de La Rioja for his research contract "Ramón y Cajal". M. Montiel thanks the C.A.R. for a grant.

Notes and references

‡ *Crystal data* for **2**: $C_{54}H_{72}Ag_4AuCl_4F_{21}N_2O_{10}$, monoclinic, $P2_1/n$, $a = 19.2046(2)$, $b = 17.4577(2)$, $c = 24.2007(3)$ Å, $\beta = 101.637(1)°$, $V = 7946.95(16)$ Å^3, $Z = 4$, $\mu = 3.038$ mm^{-1}, 75235 reflections, $2\theta_{max}$ 56°, 16737 unique ($R_{int} = 0.0441$), $R = 0.0512$, $R_w = 0.1492$ for 873 parameters, 211 restrictions, $S = 1.046$, max. $\Delta\rho = 3.225$ e Å^{-3}. Crystal data of **2** were measured at −100 °C using a Nonius KappaCCD diffractometer, Mo-Kα radiation, ω and ϕ-scans. The structure was solved by direct methods and refined anisotropically on F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen) Absorption correction: multiscan. *Special refinement details*: the structure contains extensive regions of badly resolved residual electron density, in which no solvent molecules could be clearly identified. For this reason no solvent was included in the refinement, and the formula and related information (*M*, *etc.*) do not include solvent. CCDC reference number 254889. See http://www.rsc.org/suppdata/dt/b5/b502701m/ for crystallographic data in CIF or other electronic format.

1 (*a*) *Gold: Progress in Chemistry, Biochemistry and Technology*, ed. H. Schmidbaur, John Wiley & Sons, Inc., New York, 1999; (*b*) H. Schmidbaur, *Nature*, 2001, **413**, 31; (*c*) H. Schmidbaur, *Gold Bull.*, 1990, **23**, 11.

2 (*a*) M. Bardají and A. Laguna, *Eur. J. Inorg. Chem.*, 2003, 3069; (*b*) V. J. Catalano, B. L. Bennett, M. A. Malwitz, R. L. Yson, H. M. Kar, S. Muratidis and S. J. Horner, *Comments Inorg. Chem.*, 2003, **24**, 39.

3 (*a*) M. A. Rawashdeh-Omary, M. A. Omary and J. P. Fackler, Jr., *Inorg. Chim. Acta*, 2002, **334**, 376; (*b*) O. Crespo, E. J. Fernández, M. Gil, M. C. Gimeno, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga and M. E. Olmos, *J. Chem. Soc., Dalton Trans.*, 2002, 1319; (*c*) ?V. J. Catalano and S. J. Horner, *Inorg. Chem.*, 2003, **42**, 8430; (*d*) V. J. Catalano, M. A. Malwitz and A. O. Etogo, *Inorg. Chem.*, 2004, **43**, 5714; (*e*) P. Römbke, A. Schier, H. Schmidbaur, S. Cronje and H. Raubenheimer, *Inorg. Chim. Acta*, 2004, **357**, 235.

4 (*a*) M. E. Olmos, A. Schier and H. Schmidbaur, *Z. Naturforsch., Teil B*, 1997, **52**, 203; (*b*) E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. A. Rodríguez, O. Crespo, M. C. Gimeno, A. Laguna and P. G. Jones, *Chem. Eur. J.*, 2000, **6**, 636; (*c*) J. Vicente, M. T. Chicote, M. C. Lagunas and P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1991, 1730; (*d*) J. Vicente, M. T. Chicote and M. C. Lagunas, *Inorg. Chem.*, 1993, **32**, 3748.

5 (*a*) R. Usón, A. Laguna, M. Laguna, P. G. Jones and G. M. Sheldrick, *Chem. Commun.*, 1981, 1097; (*b*) R. Usón, A. Laguna, M. Laguna, B. R. Manzano, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans*, 1984, 285; (*c*) E. J. Fernández, M. C. Gimeno, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, P. Pyykkö and D. Sundholm, *J. Am. Chem. Soc.*, 2000, **122**, 7287.

6 R. Usón, A. Laguna, M. Laguna, A. Usón, P. G. Jones and C. F. Erdbrugger, *Organometallics*, 1987, **6**, 1778.

7 M. Contel, J. Garrido, M. C. Gimeno and M. Laguna, *J. Chem. Soc., Dalton Trans.*, 1998, 1083.

8 (*a*) A. Burini, J. P. Fackler, Jr., R. Galassi, B. R. Pietroni and R. J. Staples, *Chem. Commun.*, 1998, 95; (*b*) A. Burini, R. Bravi, J. P. Fackler, Jr., R. Galassi, T. A. Grant, M. A. Omary, B. R. Pietroni and R. J. Staples, *Inorg. Chem.*, 2000, **39**, 3158.

9 (*a*) O. M. Abu-Salah and C. B. Knobler, *J. Organomet. Chem.*, 1986, **302**, C10; (*b*) M. Contel, J. Jiménez, P. G. Jones, A. Laguna and M. Laguna, *J. Chem. Soc., Dalton Trans.*, 1994, 2515.

10 E. Cerrada, M. Contel, A. D. Valencia, M. Laguna, T. Gelbrich and M. B. Hursthouse, *Angew. Chem., Int. Ed.*, 2000, **39**, 2353.

11 (*a*) A. L. Casado, J. A. Casares and P. Espinet, *Organometallics*, 1997, **16**, 5730; (*b*) A. L. Casado and P. Espinet, *Organometallics*, 1998, **17**, 3677.

12 R. Usón, A. Laguna and J. Vicente, *J. Chem. Soc., Chem. Commun.*, 1976, 353.

13 (*a*) M. U. Haque, W. Horne and O. M. Abu-Salah, *J. Crystallogr. Spectrosc. Res.*, 1992, **22**, 421; (*b*) M. S. Hussain, M. U. Haque and O. M. Abu-Salah, *J. Cluster Sci.*, 1996, **7**, 167.

14 (*a*) E. J. Fernández, A. Laguna and A. Mendía, *Inorg. Chim. Acta*, 1994, **223**, 161; (*b*) R. Usón, A. Laguna, E. J. Fernández, A. Mendía and P. G. Jones, *J. Organomet. Chem.*, 1988, **350**, 129; (*c*) R. Usón, J. Forniés, M. Tomás, J. M. Casas and R. Navarro, *J. Chem. Soc., Dalton Trans.*, 1989, 169; (*d*) R. Usón, J. Forniés, M. Tomás, J. M. Casas, F. A. Cotton, L. R. Falvello and X. Feng, *J. Am. Chem. Soc.*, 1993, **115**, 4145.

15 X. L. Lu, W. K. Leong, L. Y. Goh and A. T. S. Hor, *Eur. J. Inorg Chem.*, 2004, 2504.