Vapochromism in Complexes of Stoichiometry $[Au_2Ag_2R_4L_2]_n$

Eduardo J. Fernández[a], Antonio Laguna[b], José M. López-de-Luzuriaga[a], M. Elena Olmos[a], and Raquel C. Puelles[a]

[a] Departamento de Química, Universidad de la Rioja, Grupo de Síntesis Química de La Rioja, UA-CSIC, Complejo Científico Tecnológico, 26001 Logroño, Spain
[b] Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Reprint requests to J. M. López-de-Luzuriaga. E-mail: josemaria.lopez@unirioja.es

Z. Naturforsch. **2009**, *64b,* 1500 – 1512; received September 24, 2009

Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

Reaction of $[NBu_4][Au(C_6X_5)_2]$ (C_6X_5 = 3,5-$C_6Cl_2F_3$, C_6Cl_5) with $AgOClO_3$ in an Et_2O/CH_2Cl_2 mixture affords $[Au_2Ag_2(C_6X_5)_4(OEt_2)_2]_n$ [C_6X_5 = 3,5-$C_6Cl_2F_3$ (**1a**), C_6Cl_5 (**1b**)]. These compounds react with tetrahydrofuran, acetone, acetonitrile or toluene in solution and in the gas phase (with toluene only in solution) to the new complexes $[Au_2Ag_2(C_6X_5)_4L_2]_n$ [L = THF (**2a**, **2b**), $(CH_3)_2CO$ (**3a**, **3b**), CH_3CN (**4a**, **4b**), C_7H_8 (**5a**, **5b**)]. The crystal structures of **2a** and **5a** have been determined by X-ray diffraction methods, showing polymeric chains formed by the union of tetranuclear Au_2Ag_2 units *via* aurophilic interactions. The thermal stability and the vapochromic behaviour of these complexes have been studied by thermogravimetric analysis (TGA), X-ray powder diffraction and FT-IR spectroscopy.

Key words: Gold, Silver, Luminescence, Vapochromism

Introduction

A plethora of examples of crystal structures displaying short distances between gold(I) atoms in the solid state led Schmidbaur to coin the term aurophilicity [1]. Various examples of structural evidence for this induced some scientists to carry out theoretical studies that allowed the scientific community to accept this phenomenon in gold compounds as a standard characteristic of this element in its complexes. Aurophilicity even became a model for the description of relativistic effects in closed-shell metals, of which gold(I) is the best example [2]. This phenomenon has afterwards been extended and studied in other complexes showing metal-metal distances shorter than the sum of their van-der-Waals radii. Thus, such interactions have been found between gold(I) and other closed-shell metal atoms (Au $\cdots$ M) or even between metals different from gold with d^{10}-d^{10}, s^2-d^8 or d^8-d^{10} configurations [3 – 19]. In some cases theoretical studies of selected examples have been carried out [2], concluding that these interactions always have non-negligible contributions arising from dispersion forces reinforced by relativistic effects, which reach a maximum for the gold compounds [20]. In addition, these heterometallic complexes are interesting not only from a theoretical point of view, but also because of the photophysical properties observed in many of them [21] and their potential applications [22 – 34]. Therefore, the search of complexes with Au(I)-M (closed-shell metal ion) is one of the most active research topics in many laboratories working with this metal.

The number of gold-silver, or even more, gold-copper complexes is nowadays still scarce when compared to the number of compounds with homometallic interactions, although one should expect that the other members of the coinage metal group would be the best candidates to form heterometallic complexes with gold. In the particular case of gold-silver complexes, a number of species displaying Au(I) $\cdots$ Ag(I) interactions has recently been described. The most common strategy for their synthesis is the use of asymmetric polydentate ligands that can act as a bridge between the metal centres [20, 35, 36], 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) [20, 35b], $Ag(OClO_3)$ [36a], or $AgBF_4$ [35d]. A different synthetic strategy

0932–0776 / 09 / 1100–1500 $ 06.00

is the reaction between a donor metallic system, such as $[Au(C_6F_5)_2]^-$ [37], $[Au(CH_2PR_3)_2]^+$ [38], $[Au_2(CH_2SiMe_3)_2(\mu\text{-dppm})]$ [39] or $[Au(\mu\text{-}C^2,N^3\text{-bzim})]_3$ [40] (bzim = 1-benzylimidazolate), and the same acid Ag^+ salts as above. In particular, the use of perhalophenylgold(I) derivatives is a well-established and effective method to prepare heterometallic materials in our group. Thus, by using $[Au(C_6X_5)_2]^-$ or $[Au(C_6X_5)(tht)]$ (X = Cl, F) we were successful in achieving the formation of Au $\cdots$ Ag interactions, taking advantage of, firstly, the donor characteristics of the gold precursor, secondly, the bridging capabilities of these groups and, thirdly, the stability that these ligands confer to the complexes. For instance, complexes as the monodimensional polymers $[Au_2Ag_2(C_6F_5)_4L_2]_n$ (L = neutral ligand), the polymeric nature of which results from additional gold-gold contacts between tetranuclear units, are obtained. These interactions are also considered responsible for the optical properties of these complexes. Recently we described another interesting property of these complexes, which is their vapochromic behaviour [41], concluding that the reaction between $[Au_2Ag_2(C_6F_5)_4L_2]_n$ (L = THF, $(CH_3)_2CO$, CH_3CN, C_7H_8) and volatile organic compounds (VOCs) are substitution reactions rather than superficial adsorption processes, and that the exchange ability of the VOCs follows an order close to their boiling points.

In order to continue analysing the influence of other factors on this behaviour, as the donor characteristics of the bis(aryl)aurate groups, we have synthesised the related complexes $[Au_2Ag_2(C_6Cl_2F_3)_4L_2]_n$ and $[Au_2Ag_2(C_6Cl_5)_4L_2]_n$ (L = THF, $(CH_3)_2CO$, CH_3CN, C_7H_8) and studied their reactions with VOCs.

Results and Discussion

Synthesis and characterisation

Reaction of $[NBu_4][Au(C_6X_5)_2]$ (C_6X_5 = 3,5-$C_6Cl_2F_3$, C_6Cl_5) with equimolecular amounts of silver perchlorate in a mixture of diethyl ether and dichloromethane leads to the complexes $[Au_2Ag_2(C_6X_5)_4(OEt_2)_2]_n$ [C_6X_5 = 3,5-$C_6Cl_2F_3$ (**1a**), C_6Cl_5 (**1b**)] in high yields. Analytical and spectroscopic data of these complexes agree with the proposed stoichiometry (see the Experimental Section). Thus, their IR spectra show, among others, absorptions at 1588, 1557, 1057 and 783 cm^{-1} (**1a**) or 839 and 622 cm^{-1} (**1b**), arising from the presence of trifluorodichlorophenyl or pentachlorophenyl groups bonded to gold(I). Their mass spectra (MALDI-TOF) show signals corresponding to $[Au_2Ag(C_6Cl_2F_3)_4]^-$ at *m/z* = 1302 (10 %) and $[Au_2(C_6Cl_5)_3]^-$ at *m/z* = 1142 (25 %), with the expected isotopic distribution. Besides, the ^{19}F NMR spectrum of complex **1a** shows the pattern corresponding to two types of non equivalent fluorine atoms at −88.1 and −117.6 ppm, respectively, that appear as singlets.

These compounds are soluble in most conventional solvents (tetrahydrofuran, acetone, acetonitrile, *etc.*), and non-soluble in *n*-hexane or diethyl ether. Evaporation of the solvent from these solutions does not regenerate the initial starting products, but new species in which the solvent substitutes the ether molecules initially bonded to silver are recovered instead. Therefore, dissolution of complexes **1a** or **1b** in tetrahydrofuran, acetone, acetonitrile or toluene, evaporation of the solvent to dryness and addition of hexane allowed the synthesis of the related compounds $[Au_2Ag_2(C_6Cl_2F_3)_4L_2]_n$ (**a**) and $[Au_2Ag_2(C_6Cl_5)_4L_2]_n$ (**b**) [L = THF (**2a**, **2b**), $(CH_3)_2CO$ (**3a**, **3b**), CH_3CN (**4a**, **4b**), C_7H_8 (**5a**, **5b**)].

Similarly to the precursor complexes **1a** and **1b**, all spectroscopic and analytical data of **2**–**5** are in accordance with the proposed stoichiometries. In the case of complexes **a**, the absorptions due to the 3,5-dichlorotriflurophenyl groups in their IR spectra appear at similar frequencies as the ones in the precursor complex **1a**. The bands due to the neutral ligands in the spectra of both complexes **a** and **b** also appear at 917 (**2a**) or 922 (**2b**), 1687 (**3a**), 2305–2275 (**4a**) or 2304–2270 cm^{-1} (**4b**) for the ether, ketone, and nitrile groups, respectively, or at 760–693 (**5a**) or 765–702 cm^{-1} (**5b**), indicating the presence of the toluene molecules. All these neutral ligands are detected in the ^1H NMR spectra, which show the expected resonances. In all cases the mass spectra (MALDI-TOF), using dithranol as matrix, show fragments corresponding to the dissociation of the tetranuclear units, with the peak corresponding to the unit $[Au_2Ag(C_6Cl_2F_3)_4]^-$ (*m/z* = 1301) as the peak of highest molecular weight for all the dichlorotrifluorophenyl derivatives **a**. The homologous peak for the pentachlorophenyl complexes **b** ($[Au_2Ag(C_6Cl_5)_4]^-$ at *m/z* = 1449) appears in complexes **2b** and **5b**, while the parent peak is the one corresponding to the fragment $[Au(C_6Cl_5)_2]^-$ (*m/z* = 695).

In general all the complexes show a limited solubility in acetone or acetonitrile, which prevents the determination of their molar conductivity in solution. In

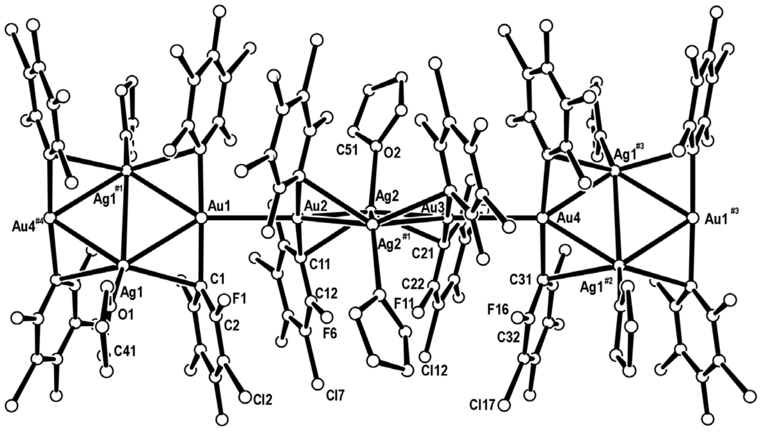

Fig. 1. Polymeric structure of complex **2a** (hydrogen atoms omitted for clarity).

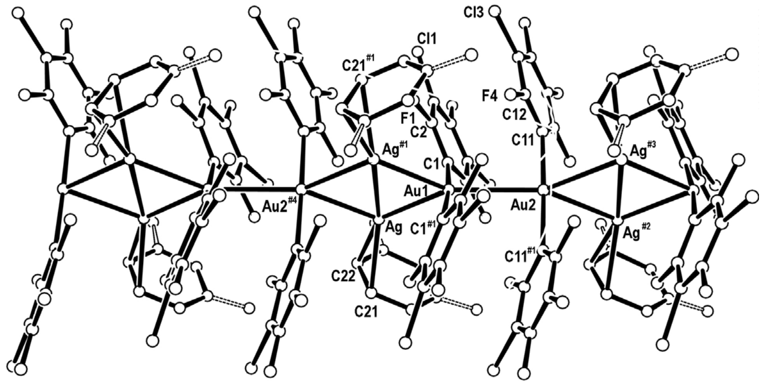

Fig. 2. Polymeric structure of complex **5a** (hydrogen atoms omitted for clarity).

addition, as will be commented below, all the neutral ligands can be at least partially substituted by acetonitrile, and therefore, the only molar conductivity measurement that could be properly determined was that of complex **4a** in acetonitrile, which, as expected, shows a typical value of 1 : 1 electrolytes.

Crystal structures of $[Au_2Ag_2(C_6Cl_2F_3)_4(THF)_2]_n$ (2a) and $\{[Au_2Ag_2(C_6Cl_2F_3)_4(\eta^2\text{-}C_7H_8)_2]\cdot C_7H_8\}_n$ (5a)

The crystal structures of complexes **2a** and **5a** were determined from single crystals obtained by slow diffusion of hexane into a solution of the complex in THF (**2a**) or toluene (**5a**). As all the structures previously described for related derivatives of formula $[Au_2Ag_2(C_6F_5)_4L_2]_n$ (L = SC_4H_8 [37a], C_6H_6 [37b], Me_2CO [37c], THF [41] or NCMe [42]), both complexes crystallise in the monoclinic space group $C2/c$ and consist of tetranuclear $[Au_2Ag_2(C_6Cl_2F_3)_4L_2]$ units linked together *via* aurophilic contacts resulting in 1D polymers that run parallel to the crystallographic y axis (Figs. 1 and 2). The intermolecular Au–Au distances of 2.8617(7) and 2.8863(7) Å in **2a** and of 2.9092(3) Å in **5a** are appreciably shorter than those found in the related pentafluorophenyl derivates with THF (3.1959(3) Å) [41], benzene (3.013(2) Å) [37b] or acetone (3.1674(11) Å) [37c] as ligands bonded to silver and closer to those described for $[Au_2Ag_2(C_6F_5)_4(SC_4H_8)_2]_n$ [37a] (2.889(2) Å) or $[Au_2(C_6F_5)_4M_2(NCMe)_2]$ (M = Ag (2.8807(4) Å), Cu (2.9129(3) Å)) [42], suggesting a substantial bonding interaction between the gold centres. In addition to the intermolecular Au$\cdots$Au contacts, there are also argentophilic intramolecular interactions within the Au_2Ag_2 core, displaying Ag–Ag distances of 3.0700(14) and 3.1487(14) Å (**2a**) or 3.0401(7) Å (**5a**), which are in general shorter than in the related pentafluorophenyl complexes of 3.2291(6) Å in the THF species [41] or 3.070 Å in the benzene derivative [37b].

The gold(I) atoms are linearly coordinated to two perhalophenyl groups with typical Au–C distances

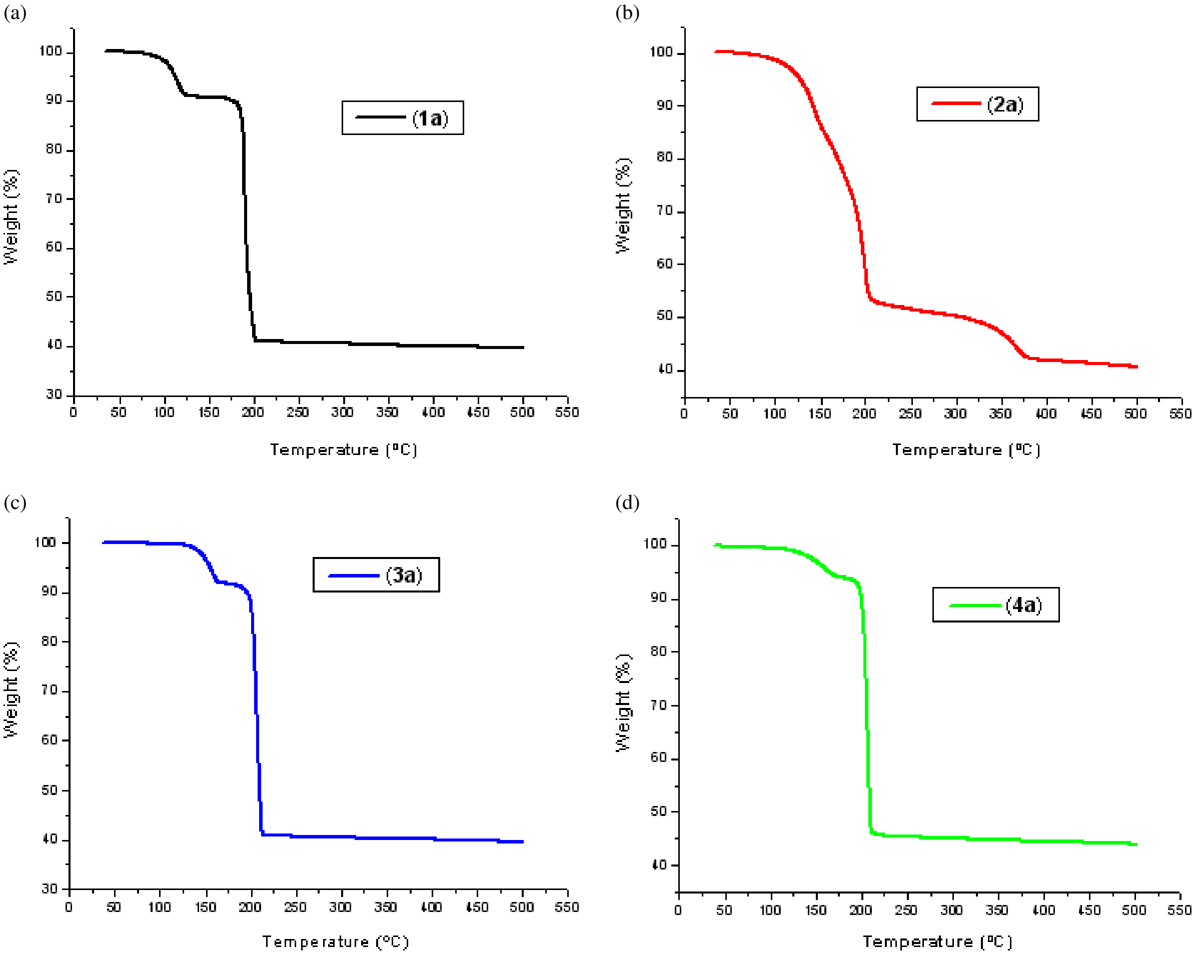

Fig. 3. TGA traces for complexes **1a** (left, above) (black), **2a** (right, above) (red), **3a** (left, below) (blue), and **4a** (right, below) (green) (colour online).

(from 2.052(8) to 2.079(8) Å in **2a** and of 2.055(4) and 2.056(4) Å in **5a**) and display additional Au–Ag contacts within the tetranuclear unit between 2.7144(8) and 2.7629(8) Å in the THF (**2a**) and of 2.7003(4) and 2.7710(4) Å in the toluene derivatives (**5a**). The former distance in all cases is shorter than those found in the structures of the previously described related complexes $[Au_2Ag_2(C_6F_5)_4L_2]_n$ [37, 41, 42] (between 2.7267(5) and 2.7903(9) Å), while the latter lies within this range.

As in the other complexes of the type $[Au_2(C_6F_5)_4\text{-}Ag_2L_2]_n$ [37, 41, 42] each neutral ligand L is coordinated to one silver(I) centre. In the case of the THF derivative **2a** the Ag–O bond length, of 2.284(8) and 2.286(8) Å are shorter than in the pentafluorophenyl compounds with *O*-donor ligands, such as tetrahydrofuran (2.307(3) Å) [41] or acetone (2.537(7) Å) [37c]. The coordinated toluene molecule in **5a** (in which the methyl group is disordered over two positions) acts as η^2 ligand, showing very different Ag–C lengths of 2.422(4) and 2.534(5) Å, while in $[Au_2Ag_2(C_6F_5)_4(\eta^2\text{-}C_6H_6)_2]_n$ the coordination of the benzene is more symmetrical (Ag–C: 2.480(10) and 2.498(12) Å) [37b].

The main difference between both structures is that, while in **5a** the perhalophenyl groups interact only with gold, in **2a** the aryl groups act as asymmetrical bridges between gold and silver (Fig. 1) with Au–C distances from 2.052(8) to 2.079(8) Å and Ag–C distances from 2.463(7) to 2.593(7) Å, showing a situation similar to those described in some of the related structures [37c, 41, 42].

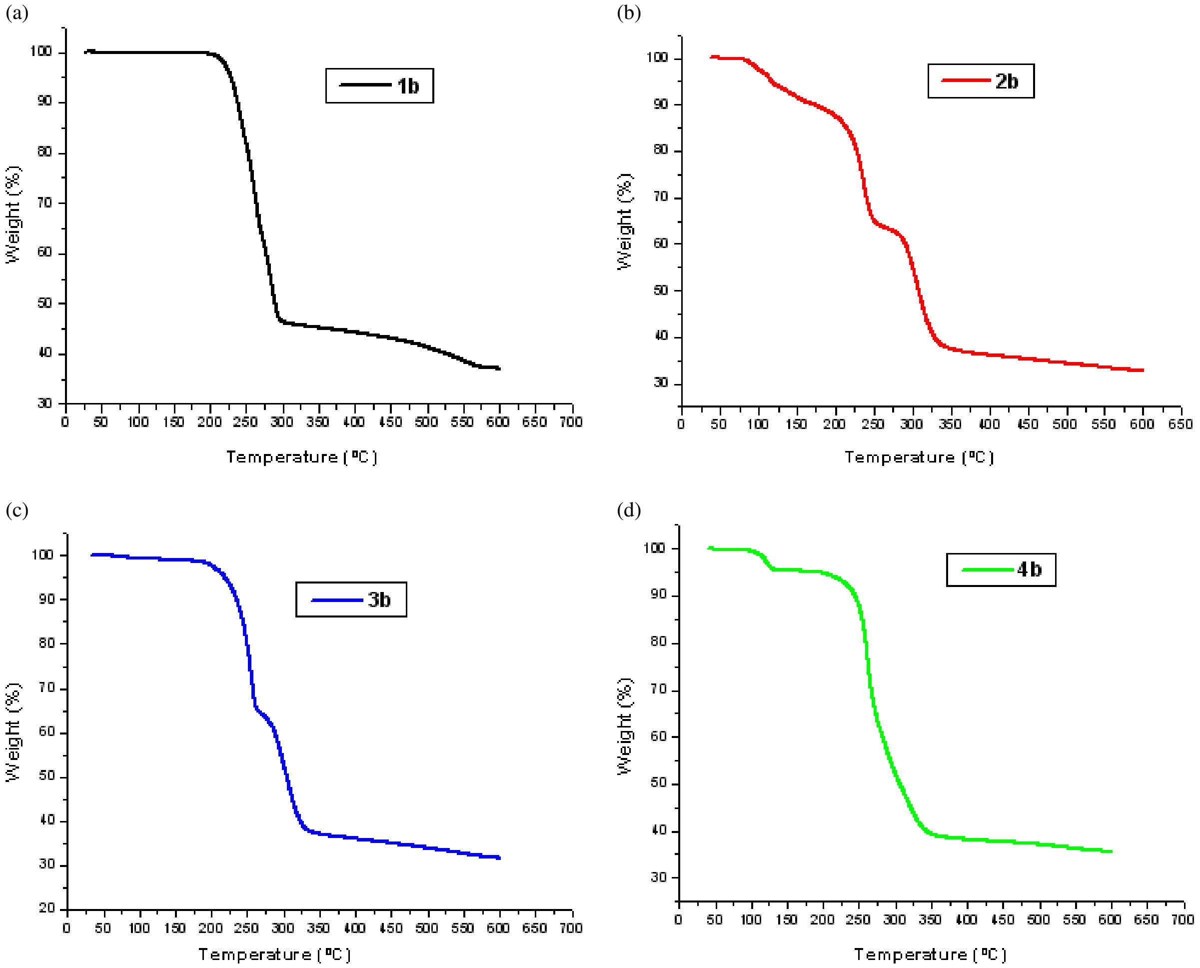

Fig. 4. TGA traces for complexes **1b** (left, above) (black), **2b** (right, above) (red), **3b** (left, below) (blue), and **4b** (right, below) (green) (colour online).

Vapochromic studies

Very interestingly, all the complexes described show perceptible changes when they are exposed to vapours of the volatile organic compounds employed as ligands for the synthesis of complexes **a** and **b**. Thus, the exposition leads to changes in the colour of the samples. This vapochromic behaviour has been studied by different techniques as, for example, thermogravimetric analyses (TGA), powder diffraction or FT-IR spectroscopy.

Thermogravimetric studies

Thermogravimetric studies of the samples obtained from the exposure of **1a** or **1b** to different organic vapours show, in general, significant differences between the TGA spectra for the $C_6Cl_2F_3$ (**a**) and the C_6Cl_5 (**b**) derivatives and are more simple than those previously reported for the related pentafluorophenyl species [41].

In complexes **a**, with the exception of the THF derivative, at a temperature of about 215 °C, nearly all of the organic material is lost, leaving an equal amount of silver and gold (Fig. 3), while in the other compounds this loss of organic material occurs at about 325 – 375 °C (**2a**, **2b**, **3b**, **4b**) or at about 550 – 575 °C (**1b**) (Fig. 4). The TGA traces for complexes **1a**, **3a** and **4a** display similar profiles, showing the loss of both molecules of Et_2O, Me_2CO or NCMe between 75 and 135 °C (**1a**) or between 120 and 175 °C (**2a** or **4a**). From 175 to 215 °C a drastic weight loss of about a 50 % is observed, corresponding to the loss of the

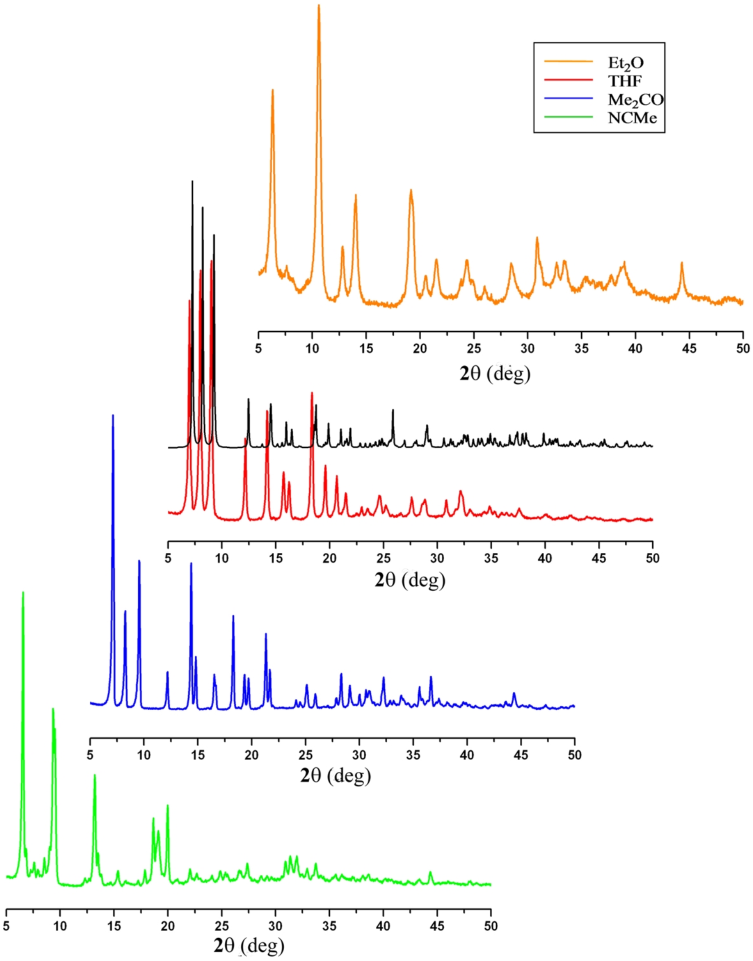

Fig. 5. XPD diffraction patterns for VOC Au-Ag materials obtained by treatment of **1a** (orange) with THF (red), acetone (blue) and acetonitrile (green) (colour online).

four perhalophenyl substituents as $HC_6F_3Cl_2$, due a reductive elimination, which has also been detected by gas-mass spectrometry. In the TGA trace of **2a** the first slope (between 75 and 215 °C) corresponds to the loss of the THF molecules and three of the four aryl groups in the form of $HC_6Cl_2F_3$ or $C_6Cl_2F_3$-$C_6Cl_2F_3$ (or both), and the remaining perhaloaryl group is lost between 215 and 375 °C as $HC_6Cl_2F_3$.

In the case of complexes **b** they all display different behaviour with increasing temperature (Fig. 4), and thus the TGA curve for the diethyl ether complex **1b** is similar to that for the tetrahydrofuran complex **2a**, showing the loss of both ether molecules and three pentacholophenyl ligands between 200 and 300 °C, while the fourth C_6Cl_5 group is lost at temperatures between 300 and 575 °C. In the case of **2b**, the TGA trace is more complex, and the first tetrahydrofuran molecule appears to be lost between 75 and 100 °C, while the second loss occurs from 120 to 180 °C. Two perhalophenyl ligands are lost between 180 and 250 °C, and the other two between 270 and 325 °C. In the acetone derivative **3b**, both acetone molecules and two perhalophenyl groups are lost between 175 and 260 °C, and the last two C_6Cl_5 groups between 270 and 325 °C. Finally, the TGA spectrum of **4b** shows the loss of both CH_3CN ligands between 100 and 130 °C, and from 200 to 350 °C the aryl ligands are lost.

From the analysis of these spectra it can be concluded that the thermal stability of the pentachlorophenyl derivatives is higher than that of the $C_6Cl_2F_3$-substituted compounds and similar to the thermal stability of the previously described pentafluorophenyl complexes [41]. The observed variations in the temperature and percentage of VOC ligands losses are likely due to their different boiling points, the

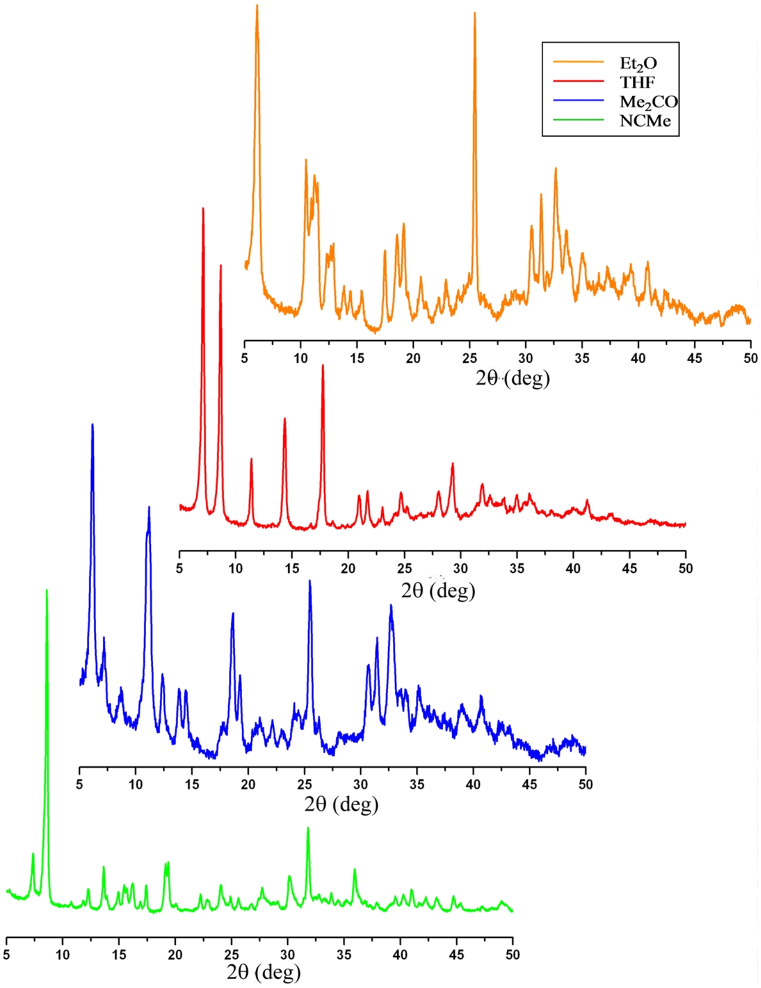

Fig. 6. XPD diffraction patterns for VOC Au-Ag materials obtained by treatment of **1b** (orange) with THF (red), acetone (blue) and acetonitrile (green) (colour online).

strengths of the interactions between the ligands with the silver centres, and the ease of VOC deprotonation (to form volatile $HC_6Cl_2F_3$ or HC_6Cl_5).

Powder diffraction studies of the vapochromic materials

X-Ray powder diffraction (XPD) studies of the materials obtained upon exposure of $[Au_2Ag_2(C_6X_5)_4(Et_2O)_2]_n$ [$C_6X_5 = C_6Cl_2F_3$ (**1a**), C_6Cl_5 (**1b**)] to different VOCs (THF, Me_2CO, CH_3CN) were carried out. First, we studied the VOCs uptake ability of diethyl ether complexes **1a** and **1b** by comparison of their XPD profiles with those obtained after exposure of **1a** or **1b** to the VOCs mentioned above. Significant differences in the profiles indicate that the substitution of the ether molecules by the different organic molecules has occurred (Figs. 5 and 6). The conclusive proof that the substitution of the Et_2O molecules is complete and not a surface adsorption process is the match of each profile with that generated from the cif file obtained from the X-ray crystal structure determination. However, this information is only available for complex $[Au_2Ag_2(C_6Cl_2F_3)_4(THF)_2]_n$ (**2a**). In this case both XPD profiles coincide.

We then studied the selectivity and reversibility of the VOCs exchange at r. t. by recording the XPD diffraction patterns of the species resulting from the exposure of each complex to the other three VOCs (Supporting information). As just explained, exposure of **1a** to any other VOC leads to the substitution of Et_2O. By contrast, the THF molecules of **2a** are only displaced upon treatment with vapours of acetone, while exposition to acetonitrile gives rise to mixtures, and treatment with Et_2O does not produce any substitu-

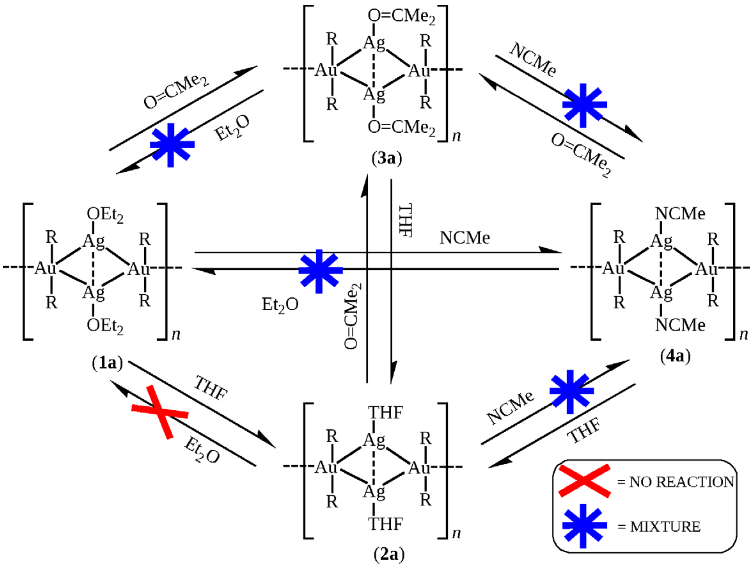

Fig. 7. Vapochromic behaviour of **1a**–**4a**.

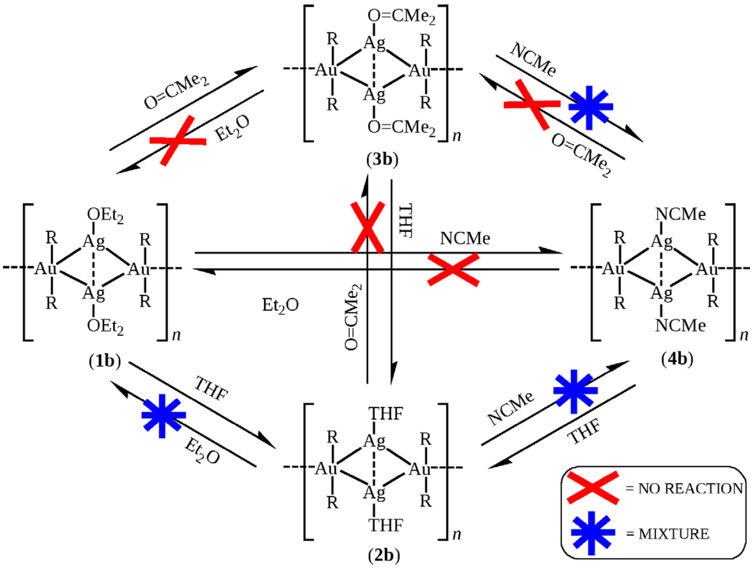

Fig. 8. Vapochromic behaviour of **1b**–**4b**.

tion (see Fig. 7). In the case of the acetone derivative **3a**, neither diethyl ether nor acetonitrile lead to the complete substitution of the organic molecules, resulting in mixtures, and only by exposition to vapours of the *O*-donor molecule THF, the Me_2CO is replaced by tetrahydrofuran. Finally, the acetonitrile molecules of **4a** can be displaced by vapours of THF or acetone, but Et_2O does not displace NCMe from the silver centres (Fig. 7). Thus, as in the pentafluorophenyl complexes [41], while diethyl ether can be displaced by the rest of VOCs, this process is not reversible. The fact that $[Au_2Ag_2(C_6F_3Cl_2)_4(NCMe)_2]_n$ (**4a**) reacts with vapours of acetone and THF, and that acetonitrile does not displace any of these *O*-donor ligands, reveal a different behaviour from that of the C_6F_5 derivatives.

A similar analysis of the vapochromic behaviour of the pentachlorophenyl compounds **1b**–**4b** leads to similar results (Fig. 8), namely that diethyl ether can be replaced by THF, Me_2CO or NCMe, but again these processes are not completely reversible. Besides, both acetone and acetonitrile are displaced from **3b** and **4b** when treated with THF in processes that are not completely reversible either. Finally, exposition of **3b** to vapours of NCMe leads to a mixture of complexes, whereas the XPD pattern of **4b** remains unchanged when exposed to Me_2CO vapours (see Supporting Information).

FT-IR studies

Exposure of **1a** or **1b** to THF, Me_2CO or NCMe vapours lead, in all cases, to compounds whose FT-IR spectra clearly show, apart from the bands corresponding to the aryl groups, the characteristic absorptions of the functional groups of the VOCs employed, which appear displaced with respect to those observed for the free VOCs, probably as a consequence of the coordination of the organic molecules to the silver atoms that weakens the C–O or N–C bonds. This, in agreement with the previously commented XPD results, suggests a complete substitution of the ether molecules in **1a** or **1b**, resulting in the same species as obtained in solution (**2**–**4**). Thus, exposition of **1a** or **1b** to THF affords compounds with δ(C–O–C) at 917 (**1a**) or 922 (**1b**) cm^{-1}. When the VOC employed is acetone the products show the ν(C=O) band at 1687 (**1a**) or 1698 (**1b**) cm^{-1}, and when NCMe is used the ν(C≡N) bands appear at 2305 and 2275 (**1a**) or at 2304 and 2270 (**1b**) cm^{-1}.

In this case it is not possible to establish a clear exchange sequence neither according to the donor ability of the VOCs bonded to silver nor to their vapour pressure, since none of these factors seem to have an effect on the susbtitution. However, from the results of our experiments it an be concluded that, as the electronegativity of the halogen atoms present in the aryl group decreases, the strength of the Ag–O bond increases, which is in accordance with the Ag-O distance found in the crystal structures of the THF derivatives, which is shorter in the 3,5-$C_6Cl_2F_3$ complex **2a** than in the C_6F_5 complex. The Au-Ag distances are also longer in the C_6F_5 derivative, which seems to indicate a higher donor ability for the bis(aryl) aurate(I) anion in the 3,5-$C_6Cl_2F_3$ complex. Therefore, the substituents present in the aryl groups, and the donor ability of the $[Au(C_6X_5)_2]^-$ anions seem to play the key role.

Experimental Section

Instrumentation

Infrared spectra were recorded in the 4000–200 cm^{-1} range on a Nicolet Nexus FT-IR spectrometer using Nujol mulls between polyethylene sheets. C, H and N analyses were carried out with a Perkin-Elmer 240C microanalyser. Mass spectra were recorded on a HP59987 A electrospray or a Microflex MALDI-TOF Bruker spectrometer operating in the linear and reflector modes using dithranol as matrix. ^1H and ^{19}F NMR spectra were recorded on a Bruker ARX 300 instrument in $CDCl_3$ solutions at r. t. Chemical shifts are quoted relative to $SiMe_4$ (^1H, external) and $CFCl_3$ (^{19}F, external). Absorption spectra in solution were recorded on a Hewlett-Packard 8453 diode array UV/Vis spectrophotometer. Thermogravimetric analyses (TGA) were recorded on a TA Instrument SDT 2960 using 2–10 mg samples at a 10 °C/min rate between 40 and 600 °C under nitrogen, and between 600 and 750 °C in air. X-Ray powder diffraction patterns were obtained at r. t. using a Rigaku D/MAX 2500 X-ray powder diffractometer equipped with graphite-monochromatised CuK_α radiation operating at 40 kV and 80 mA. Powder diffraction patterns were collected between 2θ of 5° and 60° with a 2θ stepping angle of 0.03° and an angle dwell of 1 s.

General Comments

Complexes $NBu_4[AuR_2]$ (R = $C_6Cl_2F_3$, C_6Cl_5) [43, 44] were synthesised according to literature procedures, and $[Au_2Ag_2(C_6Cl_5)_4(Me_2CO)_2]_n$ [45] was obtained following the alternative procedure described below. Solvents used in the spectroscopic studies were degassed prior to use. All the volatile organic compounds are commercially available and were purchased from Panreac. The solid-vapour reactions were carried out at r. t. by passing a stream of nitrogen gas over the liquid VOC and the VOC-saturated nitrogen over the sample.

*Synthesis of $[Au_2Ag_2R_4(OEt_2)_2]_n$ [R = 3,5-$C_6Cl_2F_3$ (**1a**), C_6Cl_5 (**1b**)]*

To a CH_2Cl_2/Et_2O solution (1 : 2) of $NBu_4[AuR_2]$ (R = 3,5-$Cl_2C_6F_3$, 0.126 g; C_6Cl_5, 0.141 g, 0.150 mmol) was added $Ag(OClO_3)$ (0.031 g, 0.150 mmol). An orange (**1a**) or deep-yellow solid (**1b**) was immediately formed and filtered after 30 min of stirring.

1a: Yield: 0.202 g, 87 %. – FT-IR (Nujol mull): $\nu(C_6Cl_2F_3)$ = 1588, 1557, 1057, 783 cm^{-1}. – ^1H NMR (300.13 MHz, 298 K, $CDCl_3$, ppm): δ = 3.37 (q, 2H, ^2J(H-H) = 7 Hz, CH_2), 1.08 (t, 3H, ^2J(H-H) = 7 Hz, Me). – ^{19}F NMR (282.4 MHz, 298 K, $CDCl_3$, ppm): δ = −88.1 (s, 2F, F_o), −117.6 (s, 1F, F_p). – MS((–)-ES): *m/z* (%) = 596 (100) $[Au(C_6F_3Cl_2)_2]^-$, 1302 (10) $([Au_2Ag(C_6F_3Cl_2)_4]^-$. – Elemental anal. for $C_{32}H_{20}Au_2Ag_2Cl_8F_{12}O_2$: calcd. C 24.67, H 1.29; found C 24.86, H 1.73.

1b: Yield: 0.221 g, 84 %. – FT-IR (Nujol): $\nu(C_6Cl_5)$ = 839, 622 cm^{-1}. – ^1H NMR (300.13 MHz, 298 K, $CDCl_3$, ppm): δ = 3.20 (m, 2H, ^2J(H-H) = 7 Hz, CH_2), 1.00 (t, 3H, ^2J(H-H) = 7 Hz, Me). – MS (MALDI-TOF (DIT)): *m/z* (%) =

Table 1. Details of data collection and structure refinement for complexes **2a** and **5a**.

Compound	**2a**	**5a**
Chemical Formula	$C_{32}H_{16}Ag_2Au_2$-$Cl_8F_{12}O_2$	$C_{38}H_{16}Ag_2Au_2$-$Cl_8F_{12} \cdot C_7H_8$
Crystal colour	orange	yellow
Crystal size, mm^3	$0.2 \times 0.08 \times 0.08$	$0.45 \times 0.07 \times 0.07$
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$
a, Å	22.4647(5)	27.0403(4)
b, Å	14.7540(3)	7.4579(1)
c, Å	25.4170(6)	23.8375(4)
β, deg	106.890(1)	102.5885(6)
V, Å^3	1048.54(5)	4691.60(12)
Z	8	4
Dc, g cm^{-3}	2.56	2.38
$F(000)$, e	5760	3148
T, K	173(2)	173(2)
$2\theta_{max}$, deg	56	59
$\mu(MoK_\alpha)$, mm^{-1}	8.8	14.2
Refl. measured / unique	31188 / 9585	35532 / 5780
R_{int}	0.0672	0.0558
Refined parameters	525	329
Restraints	156	102
R^a $[I \geq 2\sigma(I)]$	0.0531	0.0307
wR^b (F^2, all refl.)	0.1559	0.0692
S^c	1.038	1.036
Max. residual electron density, e Å^{-3}	3.34	1.35

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR(F^2) = [\Sigma\{w(F_o{}^2 - F_c{}^2)^2\} / \Sigma\{w(F_o{}^2)^2\}]^{0.5}$, $w^{-1} = \sigma^2(F_o{}^2) + (aP)^2 + bP$, where $P = [F_o{}^2 + 2F_c{}^2]/3$ and a and b are constants adjusted by the program; [c] $S = \text{GoF} = [\Sigma\{w(F_o{}^2 - F_c{}^2)^2\}/(n-p)]^{0.5}$, where n is the number of data and p the number of parameters.

Table 2. Selected bond lengths (Å) and angles (deg) for complex **2a**[a].

Au(1)–C(1)	2.076(7)	Au(3)–Au(4)	2.8617(7)
Au(2)–C(11)	2.079(8)	Au(1)–Ag(1)	2.7505(8)
Au(3)–C(21)	2.071(8)	Au(2)–Ag(2)	2.7172(8)
Au(4)–C(31)	2.052(8)	Au(3)–Ag(2)	2.7629(8)
Ag(1)–O(1)	2.284(8)	Au(4)–Ag(1)$^{\#2}$	2.7144(8)
Ag(2)–O(2)	2.286(8)	Ag(1)–Ag(1)$^{\#1}$	3.0700(14)
Au(1)–Au(2)	2.8863(7)	Ag(2)–Ag(2)$^{\#1}$	3.1487(14)
C(1)-Au(1)-C(1)$^{\#1}$	178.5(4)	C(21)-Au(3)-C(21)$^{\#1}$	179.5(4)
C(11)-Au(2)-C(11)$^{\#1}$	176.6(4)	C(31)-Au(4)-C(31)$^{\#1}$	174.7(4)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1, y, -z+1/2$; $^{\#2}$ $-x+1, y+1, -z+1/2$; $^{\#3}$ $x, y+1, z$; $^{\#4}$ $x, y-1, z$.

Table 3. Selected bond lengths (Å) and angles (deg) for complex **5a**[a].

Au(1)–C(1)	2.055(4)	Au(1)–Au(2)	2.9092(3)
Au(2)–C(11)	2.056(4)	Au(1)–Ag	2.7003(4)
Ag–C(21)	2.534(5)	Au(2)–Ag$^{\#2}$	2.7710(4)
Ag–C(22)	2.422(4)	Ag–Ag$^{\#1}$	3.0401(7)
C(1)–Au(1)–C(1)$^{\#1}$	174.6(2)	C(11)–Au(2)–C(11)$^{\#1}$	178.40(19)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, y, -z+1/2$; $^{\#2}$ $x, y+1, z$; $^{\#3}$ $-x, y+1, -z+1/2$; $^{\#4}$ $x, y-1, z$.

695 (100) $[Au(C_6Cl_5)_2]^-$, 1142 (25) $[Au_2(C_6Cl_5)_3]^-$. – Elemental anal. for $C_{32}H_{20}Au_2Ag_2Cl_{20}O_2$: calcd. C 21.90, H 1.15; found C 21.92, H 1.12.

*Synthesis of $[Au_2Ag_2R_4L_2]_n$ [R = 3,5-$C_6Cl_2F_3$, L = THF (**2a**), Me_2CO (**3a**), NCMe (**4a**), η^2-C_7H_8 (**5a**); R = C_6Cl_5, L = THF (**2b**), Me_2CO (**3b**), NCMe (**4b**), η^2-C_7H_8 (**5b**)]*

A solution of **1a** (0.156 g, 0.150 mmol) in THF (**2a**), NCMe (**4a**) or a suspension in Me_2CO (**3a**) or toluene (**5a**) or a suspension of **1b** (0.176 g, 0.1 mmol) in THF (**2b**), acetone (**3b**), acetonitrile (**4b**) or toluene (**5b**) (15 mL) was stirred for 15 min. Evaporation of the solvent to dryness gave an orange (**2a**, **3a**, **5a**), yellow (**4a**, **5b**) deep-red (**2b**, **3b**) or white (**4b**) solid in an almost quantitative yield.

2a: FT-IR (Nujol mull): $\nu(C_6Cl_2F_3)$ = 1588, 1557, 1060, 784 cm^{-1}; ν(C-O-C) = 917 cm^{-1}. – ^{1}H NMR (300.13 MHz, 298 K, $CDCl_3$, ppm): δ = 3.65 (m, 2H, CH_2O), 1.74 (m, 2H, CH_2). – ^{19}F NMR (282.4 MHz, 298 K, $CDCl_3$, ppm): δ = −88.1 (s, 2F, F_o), −117.5 (s, 1F, F_p). – MS ((+)-ES): *m/z* (%) = 507 (45) $[AuAg(C_6Cl_2F_3)]^+$. – MS ((–)-ES): *m/z* (%) = 597 $[Au(C_6Cl_2F_3)_2]^-$ (59), 1301 (100) ($[Au_2Ag(C_6Cl_2F_3)_4]^-$. – Elemental anal. for $C_{32}H_{16}Au_2Ag_2Cl_8F_{12}O_2$: calcd. C 24.74, H 1.03; found C 24.59, H 0.79.

2b: FT-IR (Nujol mull): $\nu(C_6Cl_5)$ = 837, 621 cm^{-1}; ν(C-O-C) = 922 cm^{-1}. – ^{1}H NMR (300.13 MHz, 298 K, $CDCl_3$, ppm): δ = 3.73 (m, 2H, CH_2O), 1.84 (m, 2H, CH_2). – MS (MALDI-TOF (DIT)): *m/z* (%) = 695 (100) $[Au(C_6Cl_5)_2]^-$, 1449 (21) $[Au_2Ag(C_6Cl_5)_4]^-$. – Elemental anal. for $C_{32}H_{16}Au_2Ag_2Cl_{20}O_2$: calcd. C 21.95, H 0.92; found C 22.02, H 0.89.

3a: FT-IR (Nujol mull): $\nu(C_6Cl_2F_3)$ = 1589, 1558, 1061, 784 cm^{-1}; ν(C=O) = 1687 cm^{-1}. – ^{1}H NMR (300.13 MHz, 298 K, $CDCl_3$, ppm): δ = 2.14 (s, 3H, CH_3). – ^{19}F NMR (282.4 MHz, 298 K, $CDCl_3$, ppm): δ = −88.2 (s, 2F, F_o), −117.8 (s, 1F, F_p). – MS ((-)-ES): *m/z* (%) = 600 (100) $[Au(C_6Cl_2F_3)_2]^-$, 1302 (35) $[Au_2Ag(C_6Cl_2F\ _3)_4]^-$. – Elemental anal. for $C_{30}H_{12}Au_2Ag_2Cl_8F_{12}O_2$: calcd. C 23.61, H 0.78; found C 23.50, H 0.60.

3b: FT-IR (Nujol mull): $\nu(C_6Cl_5)$ = 837, 624 cm^{-1}; ν(C=O) = 1695 cm^{-1}. – ^{1}H NMR (300.13 MHz, 298 K, $CDCl_3$, ppm): δ = 2.16 (s, 3H, CH_3). – MS (MALDI-TOF (DIT)): *m/z* (%) = 695 (100) $[Au(C_6Cl_5)_2]^-$. – Elemental anal. for $C_{30}H_{12}Au_2Ag_2Cl_{20}O_2$: calcd. C 20.91, H 0.70, found C 20.32, H 0.68.

4a: FT-IR (Nujol mull): $\nu(C_6Cl_2F_3)$ = 1590, 1558, 1060, 784 cm^{-1}; ν(C≡N) = 2305, 2275 cm^{-1}. – ^{1}H NMR (300.13 MHz, 298 K, $CDCl_3$, ppm): δ = 2.00 (s, 3H, CH_3). – ^{19}F NMR (282.4 MHz, 298 K, $CDCl_3$, ppm): δ = −88.1 (s, 2F, F_o), −117.6 (s, 1F, F_p). – MS ((–)-ES): *m/z* (%) = 600 (100) $[Au(C_6Cl_2F_3)_2]^-$, 1302 (25) $[Au_2Ag(C_6Cl_2F_3)_4]^-$. – Λ_M (acetonitrile): 124.9 mol^{-1} cm^2 Ω^{-1} (1 : 1). – Elemental anal. for $C_{28}H_6Au_2Ag_2Cl_8F_{12}N_2$: calcd. C 22.55, H 0.40, N 1.88; found C 22.73, H 0.60, N 1.64.

4b: FT-IR (Nujol mull): $\nu(C_6Cl_5)$ = 838, 615 cm^{-1}; $\nu(C{\equiv}N)$ = 2304, 2270 cm^{-1}. – ^1H NMR (300.13 MHz, 298 K, $CDCl_3$, ppm): δ = 2.20 (s, 3H, CH_3). – MS (MALDI-TOF (DIT)): *m/z* (%) = 695 (100) $[Au(C_6Cl_5)_2]^-$. – Elemental anal. for $C_{28}H_6Au_2Ag_2Cl_{20}N_2$: calcd. C 20.01, H 0.36, N 1.67; found C 19.91, H 0.36, N 1.66.

5a: FT-IR (Nujol mull): $\nu(C_6Cl_2F_3)$ = 1590, 1558, 1058, 781 cm^{-1}; $\nu(C_7H_8)$ = 760, 693 cm^{-1}. – ^1H NMR (300.13 MHz, 298 K, $CDCl_3$, ppm): δ = 7.25 (m, 2H, H_m), 7.18 (m, 3H, $H_{o/p}$), 2.34 (s, 3H, CH_3). – ^{19}F NMR (282.4 MHz, 298 K, $CDCl_3$, ppm): δ = −88.1 (s, 2F, F_o), −117.6 (s, 1F, F_p). – MS ((–)-ES): *m/z* (%) = 600 (100) $[Au(C_6Cl_2F_3)_2]^-$. – Elemental anal. for $C_{38}H_{16}Au_2Ag_2Cl_8F_{12}$: calcd. C 28.64, H 1.01; found C 29.69, H 1.14.

5b: FT-IR (Nujol mull): $\nu(C_6Cl_5)$ = 838, 621 cm^{-1}; $\nu(C_7H_8)$ = 765, 702 cm^{-1}. – ^1H NMR (300.13 MHz, 298 K, $CDCl_3$, ppm): δ = 7.22 (m, 2H, H_m), 7.17 (m, 3H, $H_{o/p}$), 2.34 (s, 3H, CH_3). – MS (MALDI-TOF (DIT)): *m/z* (%) = 695 (100) $[Au(C_6Cl_5)_2]^-$, 1449 (5) $[Au_2Ag(C_6Cl_5)_4]^-$. – Elemental anal. for $C_{38}H_{16}Au_2Ag_2Cl_{20}$: calcd. C 25.48, H 0.90; found C 25.57, H 0.92.

Crystal structure analyses

Crystals were mounted in inert oil on glass fibers and transferrred to the cold gas stream of a Nonius Kappa CCD diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected using graphite-monochromatised MoK_α radiation (λ = 0.71073 Å). Scan type: ω and ϕ. Absorption corrections: numerical (based on multiple scans). The structures were solved by Direct Methods and refined on F^2 using SHELXS/L-97 [46]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. The methyl group of the coordinated toluene molecules in **5a** are disordered over two different positions (50 : 50). Further details of the data collection and refinement are given in Table 1. Selected bond lengths and angles are collected in Tables 2 and 3.

CCDC 747549 and 747550 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request /cif.

Supporting Information

XPD diffraction patterns of the species resulting from the exposure of each complex to the other three VOCs (Figs. S1 and S2) are available as Supporting Information (online only).

Acknowledgements

This work was supported by the D. G. I.(MEC)/FEDER (CTQ2007-67273-C02-02). R. C. P. thanks the Spanish MEC for a grant.

[1] H. Schmidbaur, W. Graf, G. Müller, *Angew. Chem.* **1988**, *100*, 439 – 441; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417 – 419.

[2] P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597 – 636.

[3] a) H. H. Karsch, U. Schubert, *Z. Naturforsch.* **1982**, *37b*, 186; b) T. Tsuda, S. Ohba, M. Takahashi, M. Ito, *Acta Crystallogr.* **1989**, *C 45*, 887 – 890; c) M. Jansen, *Angew. Chem.* **1987**, *99*, 1136 – 1149; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098 – 1110.

[4] A. Heine, R. Herbst-Irmer, D. Stalke, *J. Chem. Soc., Chem. Commun.* **1993**, 1729 – 1731.

[5] H. Schmidbaur, H.-J. Öller, D. L. Wilkinson, B. Huber, G. Müller, *Chem. Ber.* **1989**, *122*, 31 – 36.

[6] S. Otsuka, *J. Organomet. Chem.* **1980**, *200*, 191 – 205.

[7] Y. Pan, J. T. Mage, M. J. Fink, *J. Am. Chem. Soc.* **1993**, *115*, 3842 – 3843.

[8] a) T. Tanase, Y. Kudo, M. Ohno, K. Kobayashi, Y. Yamamoto, *Nature* **1990**, *344*, 526; b) N. M. Boag, M. Green, J. A. K. Howard, F. G. A. Stone, H. Wadepohl, *J. Chem. Soc., Dalton Trans.* **1981**, 862 – 872.

[9] a) R. Blom, H. Werner, J. Wolf, *J. Organomet. Chem.* **1988**, *354*, 293 – 299; b) H. Pritzkow, P. Jennische, *Acta Chem. Scand.* **1975**, *A29*, 60 – 70; c) B. Krebs, H. Greiwing, *Z. Anorg. Allg. Chem.* **1992**, *616*, 145 – 153.

[10] L. A. Bengtsson, R. Hoffmann, *J. Am. Chem. Soc.* **1993**, *115*, 2666 – 2676.

[11] J. K. Nagle, A. L. Balch, M. M. Olmstead, *J. Am Chem. Soc.* **1988**, *110*, 319 – 321.

[12] A. L. Balch, B. J. Davis, E. Y. Fung, M. M. Olmstead, *Inorg. Chim. Acta* **1993**, *212*, 149 – 156.

[13] A. L. Balch, J. K. Nagle, M. M. Olmstead, P. E. Reedy, Jr., *J. Am. Chem. Soc.* **1987**, *109*, 4123 – 4124.

[14] S. Wang, J. P. Fackler, Jr., C. King, J. C. Wang, *J. Am. Chem. Soc.* **1988**, *110*, 3308 – 3310.

[15] S. Wang, G. Garzon, C. King, J. C. Wang, J. P. Fackler, Jr., *Inorg. Chem.* **1989**, *28*, 4623 – 4629.

[16] J. C. Jeffery, P. A. Jelliss, F. G. A. Stone, *Inorg. Chem.* **1993**, *32*, 3943 – 3947.

[17] T. F. Carlson, J. P. Fackler, Jr., R. J. Staples, R. E. P. Winpenny, *Inorg. Chem.* **1995**, *34*, 426 – 431.

[18] H.-K. Yip, H.-M. Lin, Y. Wang, C.-M. Che, *J. Chem. Soc., Dalton Trans.* **1993**, 2939 – 2944.

[19] O. Crespo, A. Laguna, E. J. Fernández, J. M. López-de-Luzuriaga, P. G. Jones, M. Teichert, M. Monge, P. Pyykkö, N. Runeberg, M. Schütz, H.-J. Werner, *Inorg. Chem.* **2000**, *39*, 4786 – 4792.

[20] E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. A. Rodríguez, O. Crespo, M. C. Gimeno, A. Laguna, P. G. Jones, *Chem. Eur. J.* **2000**, *6*, 636 – 644.

[21] J. M. López-de-Luzuriaga in *Modern supramolecular gold chemistry; gold-metal interactions and applications* (Ed.: A. Laguna), Wiley-VCH, Weinheim, **2008**, chapter 6, pp. 347 – 401.

[22] L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.* **2000**, *122*, 2763 – 2772.

[23] a) Q. Chang, Z. Murtaza, J. R. Lakowicz, G. Rao, *Anal. Chim. Acta* **1997**, *350*, 97 – 104; b) C. J. Murphy, W. D. Drane, *Proc. SPIE – Int. Soc. Opt. Eng.* **1995**, *2388*, 266; c) C. A. Bignozzi, C. Chiorboli, M. T. Indelli, M. A. Rampi Scandola, G. Varani, F. Scandola, *J. Am. Chem. Soc.* **1986**, *108*, 7872 – 7873; d) J. R. Winkler, C. Creutz, N. Sutin, *J. Am. Chem. Soc.* **1987**, *109*, 3470 – 3471; e) F. Scandola, M. T. Indelli, *Pure Appl. Chem.* **1988**, *60*, 973 – 980; f) M. Kato, S. Yamauchi, N. Hirota, *J. Phys. Chem.* **1989**, *93*, 3422 – 3425; g) M. E. G. Poss, N. E. Katz, L. M. Baraldo, D. D. Polonuer, C. G. Colombano, J. A. Olabe, *Inorg. Chem.* **1995**, *34*, 1830 – 1835; h) E. Waldhör, J. Poppe, W. Kaim, E. H. Cutin, M. E. G. Posse, N. E. Kartz, *Inorg. Chem.* **1995**, *34*, 3093 – 3096; i) A. C. Samuels, M. K. DeArmond, *Inorg. Chem.* **1995**, *34*, 5548 – 5551; j) C. J. Timpson, C. A. Bignozzi, B. P. Sullivan, E. M. Kober, T. J. Meyer, *J. Phys. Chem.* **1996**, *100*, 2915 – 2925; k) M. A. Rampi, M. T. Indelli, F. Scandola, F. Pina, A. J. Parola, *Inorg. Chem.* **1996**, *35*, 3355 – 3361.

[24] J. K. Evju, K. R. Mann, *Chem. Mater.* **1999**, *11*, 1425 – 1433.

[25] E. A. Baldauff, J. M. Buriak, *Chem. Commun.* **2004**, 2028 – 2029.

[26] a) W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, Z. He, K.-Y. Wong, *Chem. Eur. J.* **2003**, *9*, 6155 – 6166; b) S. M. Drew, D. E. Janzen, C. E. Buss, D. I. MacEwan, K. M. Dublin, K. R. Mann, *J. Am. Chem. Soc.* **2001**, *123*, 8414 – 8415.

[27] C. E. Buss, K. R. Mann, *J. Am. Chem. Soc.* **2002**, *124*, 1031 – 1039.

[28] a) J. W. Grate, L. K. Moore, D. E. Janzen, D. J. Veltkamp, S. Kaganove, S. M. Drew, K. R. Mann, *Chem. Mater.* **2002**, *14*, 1058 – 1066; b) C. L. Exstrom, J. R. Sowa, Jr., C. A. Daws, D. Janzen, K. R. Mann, G. A. Moore, F. F. Stewart, *Chem. Mater.* **1995**, *7*, 15 – 17; c) C. A. Daws, C. L. Exstrom, J. R. Sowa, Jr., K. R. Mann, *Chem. Mater.* **1997**, *9*, 363 – 368; d) C. E. Buss, C. E. Anderson, M. K. Pomije, C. M. Lutz, D. Britton, K. R. Mann, *J. Am. Chem. Soc.* **1998**, *120*, 7783 – 7790; e) C. L. Exstrom, M. K. Pomije, K. R. Mann, *Chem. Mater.* **1998**, *10*, 942 – 945.

[29] H. V. R. Dias, H. V. K. Diyabalanage, M. A. Rawashdeh-Omary, M. A. Franzman, M. A. Omary, *J. Am. Chem. Soc.* **2003**, *125*, 12072 – 12073.

[30] E. Cariati, X. Bu, P. C. Ford, *Chem. Mater.* **2000**, *12*, 3385 – 3391.

[31] a) R. L. White-Morris, M. M. Olmstead, F. Jiang, D. S. Tinti, A. L. Balch, *J. Am. Chem. Soc.* **2002**, *124*, 2327 – 2336; b) J. C.Vickery, M. M. Olmstead, E. Y. Fung, A. L. Balch, *Angew. Chem.* **1997**, *109*, 1227 – 1229; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1179 – 1181; c) E. Y. Fung, M. M. Olmstead, J. C. Vickery, A. L. Balch, *Coord. Chem. Rev.* **1998**, *171*, 151 – 159.

[32] M. A. Mansour, W. B. Connick, R. J. Lachicotte, H. J. Gysling, R. Eisenberg, *J. Am. Chem. Soc.* **1998**, *120*, 1329 – 1330.

[33] a) E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, J. Pérez, A. Laguna, A. A. Mohamed, J. P. Fackler, Jr., *J. Am. Chem. Soc.* **2003**, *125*, 2022 – 2023; b) E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, J. Pérez, A. Laguna, F. Mendizábal, A. A. Mohamed, J. P. Fackler, Jr., *Inorg. Chem.* **2004**, *43*, 3573 – 3581.

[34] J. Lefebvre, R. J. Batchelor, D. B. Leznoff, *J. Am. Chem. Soc.* **2004**, *126*, 16117 – 16125.

[35] a) M. A. Rawashdeh-Omary, M. A. Omary, J. P. Fackler, Jr., *Inorg. Chim. Acta* **2002**, *334*, 376 – 384; b) O. Crespo, E. J. Fernández, M. Gil, M. C. Gimeno, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga, M. E. Olmos, *J. Chem. Soc., Dalton Trans.* **2002**, 1319 – 1326; c) V. J. Catalano, S. J. Horner, *Inorg. Chem.* **2003**, *42*, 8430 – 8438; d) V. J. Catalano, M. A. Malwitz, A. O. Etogo, *Inorg. Chem.* **2004**, *43*, 5714 – 5724; e) P. Römbke, A. Schier, H. Schmidbaur, S. Cronje, H. Raubenheimer, *Inorg. Chim. Acta* **2004**, *357*, 235 – 242.

[36] a) M. E. Olmos, A. Schier, H. Schmidbaur, *Z. Naturforsch.* **1997**, *52b*, 203 – 208; b) J. Vicente, M. T. Chicote, M. C. Lagunas, P. G. Jones, *J. Chem. Soc., Chem. Commun.* **1991**, 1730 – 1731; c) J. Vicente, M. T. Chicote, M. C. Lagunas, *Inorg. Chem.* **1993**, *32*, 3748 – 3754.

[37] a) R. Usón, A. Laguna, M. Laguna, P. G. Jones, G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.* **1981**, 1097 – 1098; b) R. Usón, A. Laguna, M. Laguna, B. R. Manzano, P. G. Jones, G. M. Sheldrick, *J. Chem. Soc., Dalton Trans* **1984**, 285 – 292; c) E. J. Fernández, M. C. Gimeno, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, P. Pyykkö, D. Sundholm, *J. Am. Chem. Soc.* **2000**, *122*, 7287 – 7293.

[38] R. Usón, A. Laguna, M. Laguna, A. Usón, P. G. Jones, C. F. Erdbrugger, *Organometallics* **1987**, *6*, 1778 – 1780.

[39] M. Contel, J. Garrido, M. C. Gimeno, M. Laguna, *J. Chem. Soc., Dalton Trans.* **1998**, 1083 – 1084.

[40] a) A. Burini, R. Galassi, B. R. Pietroni, J. P. Fackler, Jr., R. J. Staples, *Chem. Commun.* **1998**, 95 – 96; b) A. Burini, R. Bravi, J. P. Fackler, Jr., R. Galassi, T. A. Grant, M. A. Omary, B. R. Pietroni, R. J. Staples, *Inorg. Chem.* **2000**, *39*, 3158 – 3165.

[41] E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, R. C. Puelles, A. Laguna, A. A. Mohamed, J. P. Fackler, Jr., *Inorg. Chem.* **2008**, *47*, 8069 – 8076.

[42] E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, M. Rodríguez-Castillo, *Organometallics* **2006**, *25*, 3639 – 3646.

[43] E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, J. Pérez, R. C. Puelles, J. C. Sáenz, *J. Chem. Soc., Dalton Trans.* **2005**, 1162 – 1164.

[44] R. Usón, A. Laguna, J. Vicente, *J. Organomet. Chem.* **1977**, *131*, 471 – 475.

[45] R. Usón, A. Laguna, M. Laguna, B. R. Manzano, A. Tapia, *Inorg. Chim. Acta* **1985**, *101*, 151 – 153.

[46] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.