Gold(I)–isocyanide and gold(I)–carbene complexes as substrates for the laser decoration of gold onto ceramic surfaces†

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Gold–isocyanide complexes XAu(RNC) (X = halide, pseudohalide, R = alkyl, aryl) and water soluble gold–carbene complexes $XAuC(NHPh)[MeN(CH_2CH_2O)_nMe]$ ($X = Cl$, $n = 1–11$) have been prepared and evaluated as substrates for the direct laser writing of gold decoration onto ceramics.

Introduction

The chemistry of gold has enjoyed a renaissance over the last decade or so due to developing interests in areas as diverse as luminescent[1a,b] and nonlinear optical properties,[2a,b] drug therapy,[3a,b] and homogeneous[4] and heterogeneous catalysis.[5a,b] Another area of gold chemistry with a much longer history is that of gold decoration of ceramics and glass.[6] Developed in the 19th century, the method still used today involves application of a gold sulforesinate dissolved in an organic solvent mixture, followed by firing. The problems of dealing with volatile organic compounds during both application and firing, together with wastage of wares due to failure during the firing stage has stimulated the search for alternative procedures, amongst them MOCVD (metal–organic chemical vapour deposition). Whilst gold may be deposited by conventional MOCVD or laser induced MOCVD, these techniques have not been widely applied because of the instability and low synthetic yields of the most common precursor $Me_2Au(acac)$.[7] Hence gold films required for electronic applications are produced mainly by plating or sputtering methods.[8a,b]

We wish to report here on the preparation and use of gold(I)–isocyanide and gold(I)–carbene complexes as substrates for the laser writing of gold patterns on ceramic surfaces, thus eliminating the need for final firing. Furthermore, the gold(I)–carbene complexes which have been developed exhibit sufficient water solubility for use in laser writing, thus eliminating the need for organic solvents.

Experimental

NMR spectra were recorded using a Bruker DPX300 spectrometer at 298 K (^1H, 300 MHz; ^{13}C, 75 MHz). Chemical shifts were measured relative to tetramethylsilane (TMS) and calibrated against the residual solvent resonance. Infrared spectra were recorded on a Thermo Nicolet FT-IR spectrometer. MALDI (matrix assisted laser desorption ionisation) spectra were obtained on a Voyager-DE-STR instrument using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix material. TGA/DSC studies were performed on a Rheometric Scientific STA 1500 instrument. Surface profilometry was performed using a Planar Products SF200 Surfometer. FESEM (field emission scanning electron microscopy) photographs were obtained using an XTEK HMXST 225 instrument. Tetrahydrofuran and diethyl ether were distilled from sodium wire and dichloromethane was distilled from CaH_2. Isocyanides were prepared following literature procedures and distilled before use.[9a–d] $(Me_2S)AuCl$ was prepared using a literature procedure.[10] The polyethylene glycol monomethyl ethers $HO(CH_2CH_2O)_nMe$ ($n = 1$, 2, 3, 5 and 11 **3a–d**,**f**) were obtained commercially. The $n = 9$ compound **3e** was prepared by chain extension through the reaction of $Me(OCH_2CH_2)_7OSO_2C_6H_4Me$-*p* **4e** with the sodium alkoxide derived from diethylene glycol.[11] Wet® and Foamex® products were obtained from Goldschmidt UK Limited (Tego House, Chippenham Drive, Milton Keynes, UK MK10 0AF). Epolight® 2340 was obtained from Epolin Limited (358–364 Adams Street, Newark, New Jersey 07105, USA). ITA 324 was obtained from Emery Colours Limited (Podmore Street, Burslem, Stoke-on-Trent, UK ST6 2EZ).

A. Synthesis of (MeNC)AuCl 2a[12]

MeNC (0.7 ml) in dichloromethane (10 ml) was added dropwise to a suspension of $(Me_2S)AuCl$ (2.00 g, 6.80 mmol) in dichloromethane (50 ml) under nitrogen and maintained at room temperature in the absence of light with stirring for 4 h. After overnight refigeration, the product was filtered off and washed with petroleum ether (bp 40–60 °C) and to give (MeNC)AuCl **2a** (1.65 g, 89%) as a white solid. Other (isocyanide)AuCl complexes were prepared in the same way. A full listing of characterisation data is given in the ESI.†

B. Synthesis of (MeNC)AuBr 2b[12]

(MeNC)AuCl (0.5 g, 1.83 mmol) was suspended in dichloromethane (25 ml). With stirring, KBr (0.218 g, 1.83 mmol) dissolved in water (25 ml) was added and the biphasic system was

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† Electronic supplementary information (ESI) available: Characterising data for **4a–4g**, **5a–5f**, **6a–f**, **2a–o** and **7**. See DOI: 10.1039/b617347k

stirred for 3 h. The organic phase was separated and washed with water. After removal of solvent, the residue was recrystallised from $CHCl_3$–petroleum ether (bp 40–60 °C) to give (MeNC)AuBr **2b** as a white solid (0.489 g, 84%). Other halide and pseudohalide compounds were prepared from the analogous chloride in the same way. A full listing of characterisation data is given in the ESI.†

C. Synthesis of $Me(OCH_2CH_2)_nSO_3C_6H_4Me$-*p* ($n = 1$–$3$) 4a–c[13]

To a solution of $MeOCH_2CH_2OH$ **3a** (4.3 ml, 60 mmol) in pyridine (9.7 ml, 120 mmol) at 0 °C was added *p*-$C_6H_4MeSO_3Cl$ (12.5 g, 66 mmol). The reaction mixture was left to stir at 0 °C for 3.5 h. Toluene (100 ml) and 10% HCl (100 ml) were added. After drying the organic layer with $MgSO_4$, the solvent was removed from the organic layer to yield $MeOCH_2CH_2OSO_3C_6H_4Me$-*p* **4a** as a colourless oil (13.9 g, 100%). Compounds **4b**, **4c** ($n = 2, 3$) were prepared as viscous liquids in a similar fashion. A full listing of characterisation data is given in the ESI.†

D. Synthesis of $Me(OCH_2CH_2)_nSO_3C_6H_4Me$-*p* ($n = 5, 7, 9, 11$) 4d–g[14]

Sodium hydroxide (7.8 g, 196.0 mmol) in water (40 ml) and PEG 550 (for **4g**) (38.0 g, 70.0 mmol) in THF (40 ml) were cooled in an ice–water bath with stirring and *p*-$C_6H_4MeSO_3Cl$ (24.0 g, 126.0 mmol) in THF (40 ml) was added dropwise over 2 h. The reaction mixture was stirred for an additional 2 h at 5 °C, poured into ice–water (100 ml) and extracted with dichloromethane (2 × 50 ml). The combined organic extracts were washed with water (2 × 50 ml) and saturated sodium chloride (1 × 50 ml), dried with $MgSO_4$ and the solvent removed *in vacuo* to yield **4g** as a colourless oil (40.7 g, 99%). Compounds **4d–f** were prepared similarly. A full listing of characterisation data is given in the ESI.†

E. Synthesis of $Me(OCH_2CH_2)_nNHMe$ ($n = 1, 2, 3, 5, 9, 11$) 5a–f[11]

Compound **4a** (4.73 g, 21.88 mmol) was dissolved in 33% methylamine in ethanol (8.9 ml) and refluxed for 23 h at 74 °C. After evaporation of the solvent, the resultant residue was dissolved in 5% HCl (6 ml) and extracted with chloroform (3 × 10 ml). The chloroform extracts were washed separately with 5% HCl (2 × 8 ml) and all the HCl extracts were combined, made basic with 30% sodium hydroxide (5 ml) and extracted with chloroform (3 × 15 ml). The chloroform extracts were washed separately with water (5 ml) and the solvent was removed *in vacuo* to yield **5a** as a pale yellow oil (1.4 g, 72%). Compounds **5b–f** were prepared similarly. A full listing of characterisation data is given in the ESI.†

F. Synthesis of $XAuC(NHPh)[MeN(CH_2CH_2O)_nMe]$ ($X = Cl$, $n = 1$)[15]

Compound **5a** (1.18 g, 13.24 mmol) was added to ClAu(PhNC) **2n** (0.500 g, 1.49 mmol) in CH_2Cl_2 (100 ml) and the reaction mixture was stirred for 3 h at room temperature under N_2. The solvent was then removed to give a residue which was recrystallised from CH_2Cl_2–hexane (1 : 1) to yield **6a** as white crystals (0.20 g, 45%, mp 127–129 °C). CHN calculated C 31.1%, H 3.79%, N 6.59%; found C 30.9%, H 3.90%, N 6.46%.

The compounds $XAuC(NHPh)[MeN(CH_2CH_2O)_nMe]$ ($X = Cl$, $n = 2, 3, 5, 9, 11$; $X = Br$, $n = 5$) **6b–g** were isolated as yellow oils after purification by chromatography on silica gel 60 PF_{254} (98 : 2 chloroform–methanol eluent). A full listing of characterisation data is given in the ESI.†

G. Synthesis and crystal structure of $\{(NCS)AuC(NHMe)(NEt_2)\}_2$ 7

(NCS)Au(MeNC) **2d** (100 mg, 0.34 mmol) was dissolved in CH_2Cl_2 (20 ml) and $HNEt_2$ (0.3 ml, 2.3 mmol) was added dropwise. After stirring for 4 h, the solvent and excess $HNEt_2$ were removed under vacuum. The residual white solid was recrystallised from petroleum ether (bp 40–60 °C) to give **7** (95 mg, 78%, mp 109–110 °C). CHN calculated C 22.8%, H 3.82%, N 11.4%; found C 23.1%, H 3.65%, N 11.2%. NMR and IR data are given in the ESI.† X-Ray diffraction data for **7** were collected by means of combined phi and omega scans on a Bruker-Nonius KappaCCD area detector situated at the window of a rotating anode (λ Mo-K_α = 0.71073 Å). The structure was solved by direct methods, refined by full matrix least squares on F^2 and corrected for absorption effects. Hydrogen atoms were included in the refinement, but thermal parameters and geometry were constrained to ride on the atom to which they are bonded.

Crystal data for **7**: $C_{14}H_{28}Au_2N_6S_2$, monoclinic, $P2_1/n$, a = 7.1104(6), b = 7.5366(6), c = 19.7004(15) Å, β = 96.569(5)°, T = 150 K, U = 1048.78(15) Å^3, $Z = 2$, D_c = 2.338 Mg m^{-3}, μ = 14.180 mm^{-1}, θ_{max} = 25.02°, 3311 measured, 1635 unique (R_{int} = 0.0661) and 1213 ($I > 2\sigma(I)$) reflections, $R1$ (obs) = 0.0469 and $wR2$ (all data) = 0.1125, ρ_{max}/ρ_{min} = 2.154/−2.084 e Å^{-3}.

CCDC reference number 629185.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617347k

H. Adhesion testing to European Standard (part 4 of EN 12875)

The gold film was immersed in a static solution of a specified alkaline dishwashing detergent (containing phosphate as given in IEC (International Electrotechnical Commission), amendment 3) at 75 °C for 8 h (roughly equivalent to 75 dishwasher cycles). (Precious metal decorations are generally quite susceptible to damage during this test due to the softness of gold and attack at the bonded ceramic surface leading to peeling.) The film was then removed, washed and rubbed dry. The samples were then examined visibly in comparison to starting samples. For optimised films, there was little or no deterioration in film colourisation.

Results and discussion

A. Synthesis and characterisation of (RNC)AuX complexes

As RAu(CNMe) complexes (R = Me, CF_3, C_2R') have previously been shown to be useful precursors for conventional MOCVD,[16a,b] a variety of LAuX (L = isocyanide, X = halide, pseudohalide) compounds **2a–n** (Table 1) were prepared using ligand exchange of $(Me_2S)AuCl$ **1** followed (if necessary) by metathesis of LAuCl with the appropriate potassium halide or pseudohalide.

The thermal stability and decomposition pathway for the XAu(RNC) comlpexes have been studied by TGA/DSC (Fig. 1). The majority of the isocyanide complexes [together with

Table 1 Melting point and decomposition temperature data

	Ligand	X	Melting point/°C	Decomposition temperature/°C
2a	MeNC	Cl	[a]	210–290
2b	MeNC	Br	204	220–290
2c	MeNC	I	175	175–220
2d	MeNC	SCN	149	(a) 190–210 (b) 210–500
2e	EtNC	Cl	119	193–290
2f	EtNC	I	73	175–230
2g	^tBuNC	Cl	[a]	(a) 160–200 (b) 210–240
2h	^tBuNC	I	92	120–180
2a	cyclohexylNC	Cl	136	200–290
2j	cyclohexylNC	I	60	(a) 190–210 (b) 210–310
2k	2,6-$Me_2C_6H_3NC$	Cl	142	270–310
2l	2,6-$Me_2C_6H_3NC$	Br	134	(a) 290–350 (b) 350–550
2m	2,6-$Me_2C_6H_3NC$	I	157	(a) 200–250 (b) 250–500
2m	C_6H_5NC	Cl	181	210–290
2o	PMe_3	Cl	215	290–340
2p	Me_2S	Cl	[a]	110–160
6a	$C(NHPh)[MeNCH_2CH_2OMe]$	Cl	132	140–350
6b	$C(NHPh)[MeN(CH_2CH_2O)_2Me$	Cl	Liquid	120–250
6c	$C(NHPh)[MeN(CH_2CH_2O)_3Me$	Cl	Liquid	90–260
6d	$C(NHPh)[MeN(CH_2CH_2O)_5Me$	Cl	Liquid	260–350
6e	$C(NHPh)[MeN(CH_2CH_2O)_9Me$	Cl	Liquid	120–320
6f	$C(NHPh)[MeN(CH_2CH_2O)_{11}Me$	Cl	Liquid	120–290
AuCl	—	—	[a]	(a) 190–220 (b) 230–290

[a] Decomposes before melting.

$ClAu(Me_2S)$ and $ClAu(PMe_3)$ for comparison] decompose after melting in a single stage endothermic process corresponding to:

$$(RNC)AuX \rightarrow Au + RNC + 0.5\ X_2$$

AuCl decomposes initially to an AuCl/$AuCl_3$ eutectic mixture of composition $AuCl_{1.5}$ which then undergoes further decomposition to gold:[17]

$$2\ AuCl \rightarrow AuCl_{1.5} + 0.25\ Cl_2 + Au$$

$$AuCl_{1.5} \rightarrow Au + 0.75\ Cl_2$$

Decomposition of the ClAu(RNC) complexes occurs at a temperature very similar to the decomposition temperature of AuCl and therefore it is not possible to determine whether loss of isocyanide precedes or follows elimination of chlorine. Analysis of volatile products by pyrolysis-GC/MS shows the presence of C_6H_5NC and C_6H_5CN in a ratio of 5 : 1,[18] together with a small amount of phenylcarbonimidic acid chloride ($C_6H_5NCCl_2$). The broad decomposition process from 200–600 °C for (NCS)Au(MeNC) corresponds to decomposition of poly(thiocyanogen) which may be observed as an orange solid in the platinum crucible. Residual weights of gold are within ±5% of calculated values.

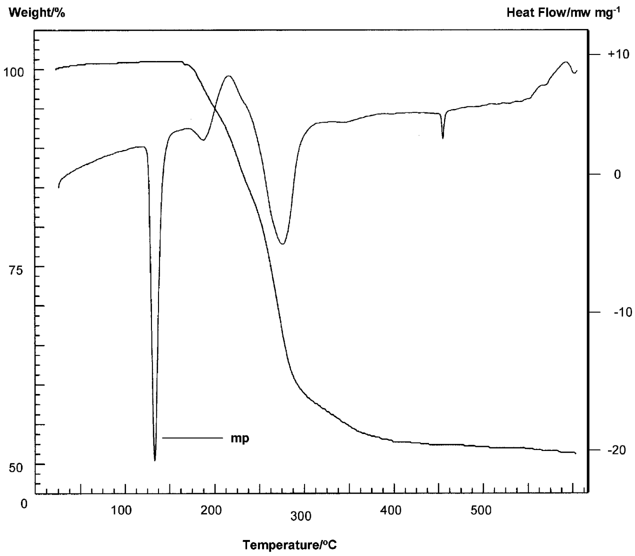
For the alkyl isocyanide series, the decomposition temperatures and melting points increase in the order $I < Br < Cl$ and in the order $^tBu < Et < Me$. For the aryl isocyanide series, both the melting points and decomposition temperatures are much higher. Laser deposition work was carried out mostly with ClAu(2,6-$Me_2C_6H_3NC$) as it exhibits the longest liquid range (140–270 °C) of all the precursors studied.

B. Synthesis, solubility and thermal stability of water soluble XAuC(NHPh)(MeNR) complexes

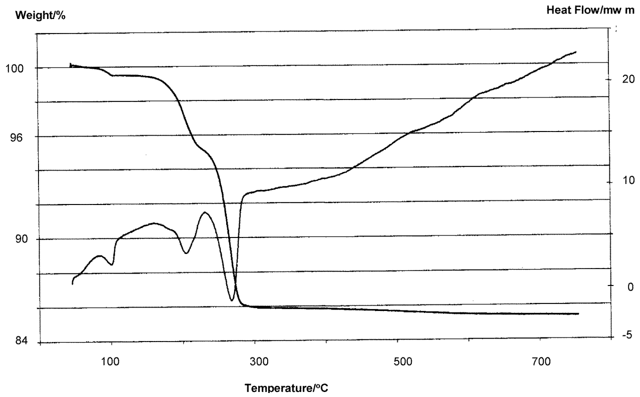
Water solubility in molecular gold(I) complexes has previously been imparted through the use of ionisable or solubilising groups in complexed ligands such as phosphines[19a–c] or (mimicking gold sulforesinates) through the introduction of ionisable groups into the thiolate residue of Au–SR complexes.[20a–c] We have chosen to use the well documented solubilising effect of poly(oxyethylene) chains to impart water solubilty through reaction of the functionalised secondary amine series $HMeN(CH_2CH_2O)_nMe$ **5a–f** with (PhNC)AuX (X = Cl, Br) **2n**,**o** to give the carbene series $XAuC(NHPh)[MeN(CH_2CH_2O)_nMe]$ **6a–g** (Scheme 1).

Whereas **6a–c** were prepared from monomethyl ethers containing single chain lengths (n = 1, 2, 3), compounds **6d–g** (n = 5, 9 and 11) were prepared from monomethyl ethers **3d–f** containing a mixture of chain lengths averaging approximately to n = 5, 9 and 11 respectively. These compounds were best characterised through their MALDI spectra which exhibit abundant $[Au(carbene)_2]^+$ ions arising from ionisation/desorption in the MALDI matrix. Thus the MALDI spectrum of $HMeN(CH_2CH_2O)_9Me$ **5e** exhibits peaks of varying intensity corresponding to the range of chain lengths n = 5 to n = 13 (Fig. 2). The MALDI spectrum of the gold complex $ClAuC(NHPh)(MeN(CH_2CH_2O)_9Me)$ **6e** prepared from **5e** shows twelve of the fifteen peaks expected for ions of composition $\{AuC(NHPh)(MeN(CH_2CH_2O)_{n_1}Me)\}\{C(NHPh)(MeN(CH_2CH_2O)_{n_2}Me\})]^+$ where $n_1 + n_2 = 10$ to 26. Other carbene complexes exhibit similar MALDI spectra.

(a) ClAuC(NHPh)(MeNCH$_2$CH$_2$OMe)



(b) AuCl



(c) BrAu(MeNC)

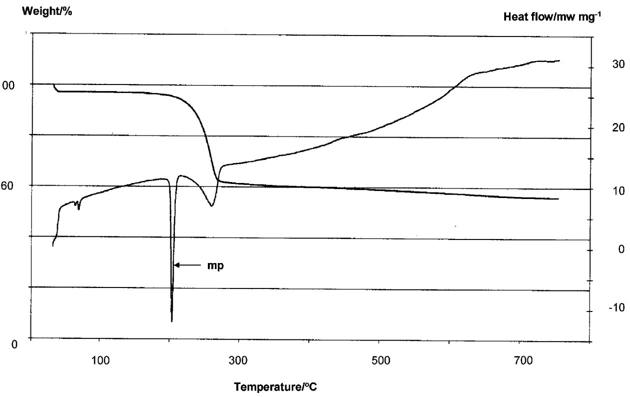
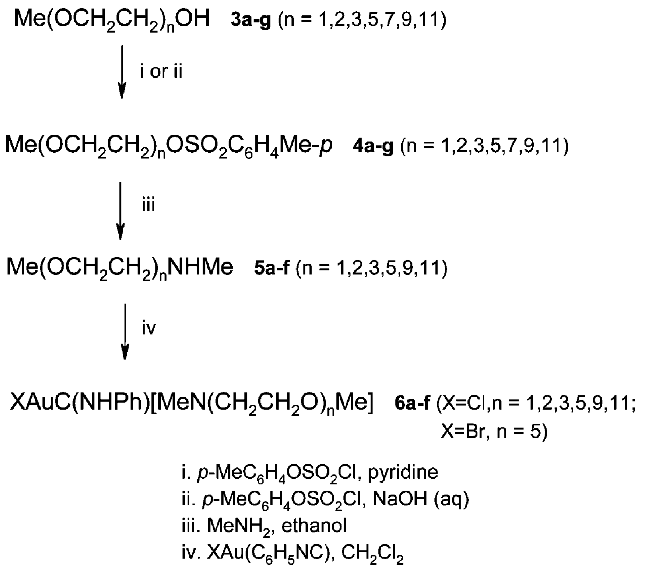
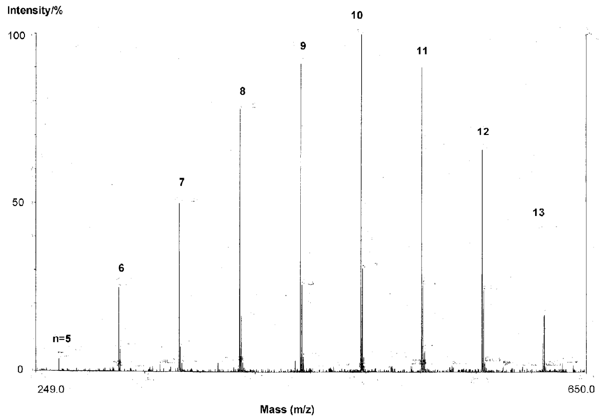


Fig. 1 TGA/DSC Traces for (a) ClAuC(NHPh)(MeNCH$_2$CH$_2$OMe), (b) AuCl and (c) BrAu(MeNC).



Scheme 1 Synthesis of XAuC(NHPh)[MeN(CH$_2$CH$_2$O)$_n$Me] compounds.

(a) MeHN(CH$_2$CH$_2$O)$_9$Me



(b) ClAuC[(NHPh)(MeN(CH$_2$CH$_2$O)$_9$Me]

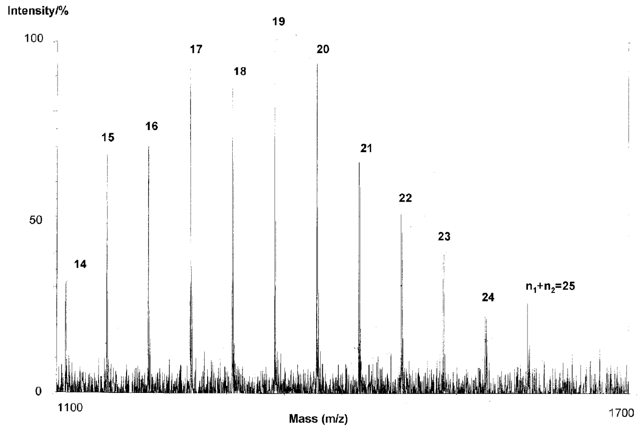
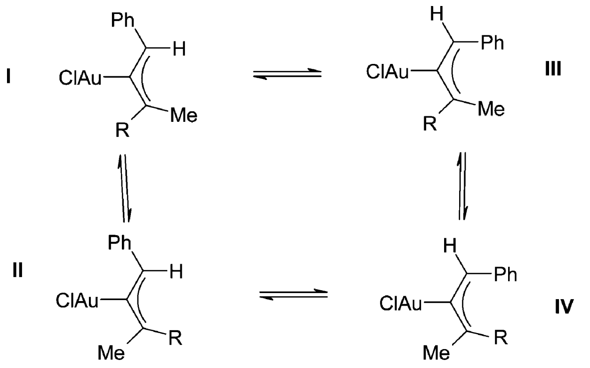


Fig. 2 MALDI Spectra of (a) MeHN(CH$_2$CH$_2$O)$_9$Me and (b) ClAuC[(NHPh)(MeN(CH$_2$CH$_2$O)$_9$Me].

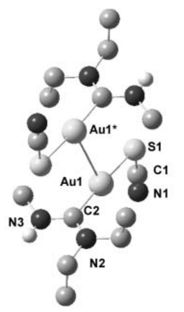
Except for **6a**, all of the gold–carbene complexes were isolated as oils which could not be crystallised. ^{13}C NMR spectra of **6a–g** all show two Au–*C* carbene resonances of approximately equal intensity in the range 185–195 ppm assignable to two of the four possible conformational isomers **I–IV** (Scheme 2). Though not interconverting fast enough to average NMR resonances, the



Scheme 2 Conformation isomerism in ClAuC(NHPh)(MeNR) complexes.

rate of interconversion is sufficiently fast to preclude chemical separation by chromatography. We have, however, characterised the solid state structure of (CNS)AuC(NHMe)(NEt$_2$) **7** prepared from the reaction of (NCS)Au(CNMe) with HNEt$_2$ (Fig. 3). In solution, this complex exhibits a single ^{1}H N–H resonance consistent with the presence of only one conformer, shown to be **I**. The methyl groups of the ethyl substituents are oriented perpendicular to the Au–C$_2$N$_2$N$_3$ plane, thus minimising their steric influence. Thus, in solution, we assign the doubling of many NMR resonances for **6a–g** to the presence of an approximately equal population of conformers **I** and **II**. The solid state structure of **7** also demonstrates the weak aurophilic interaction present in many Au^I compounds of this type.[21a–g]

Note: Au1* indicates that this atom is at equivalent position (-x,-y,-z)



Important Structural Parameters: Au1-Au1* 3.1316(10) Å; Au1-C2 2.017(11) Å; Au1-S 2.323(3) Å C2-N3 1.347(17) Å; C2-N2 1.320(16) Å; C2-Au1-S1 173.4(3) °; Au1-S1-C1N1 97.0(4) °; N3-C2-N2 118.0(11) °

Fig. 3 Molecular structure of {(CNS)AuC(NHMe)(NEt$_2$)}$_2$.

Pyrolysis-GC/MS and TGA/DSC studies of **6a** (Fig. 1) also show the production of a mixture of C$_6$H$_5$NC and C$_6$H$_5$CN, thus indicating that the primary step in the decomposition of the gold–carbene complexes is elimination of HMeN(CH$_2$CH$_2$O)$_n$Me. The residual weights of gold obtained are again within ±5% of the calculated values.

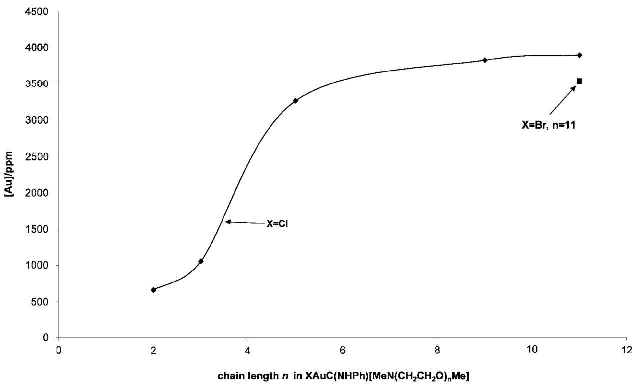


Fig. 4 Water solubility of XAuC(NHC$_6$H$_5$)[MeN(CH$_2$CH$_2$O)$_n$Me] complexes as a function of chain length.

A plot of water solubility as a function of chain length (Fig. 4) shows an initial sharp increase in solubility (n = 2–5) followed by a levelling off towards higher chain lengths (n = 9, 11). The solubility of the bromo analogue where n = 11 is almost identical to that of the chloride. Compound **6f** was chosen for most of the laser writing work due to its greater water solubility and high preparative yield.

C. Laser writing using gold–isocyanide and gold–carbene complexes[22]

A schematic diagram of the laser writing process is shown in Fig. 5. As all the gold precursors are transparent at 1064 nm (continuous wave Nd:YAG), an absorption enhancer (finely divided SiO$_2$) was used.[23] Decomposition of the gold precursor is thus photothermal, involving photochemical absorption by the enhancer followed by transfer of heat energy to cause thermal decomposition of the organogold compound. Movement of the beam head is software controlled; the key variables are power output (up to 5 W) and writing speed (up to 25 cm s^{-1}) and the hatch spacing. The nominal beam width at the focal point is 50 µm. Compounds **2k** and **6f** were chosen for most trials because of their high synthetic yield; however, other complexes in both the isocyanide and carbene series give similar deposition results. The quality of the metal film (colour

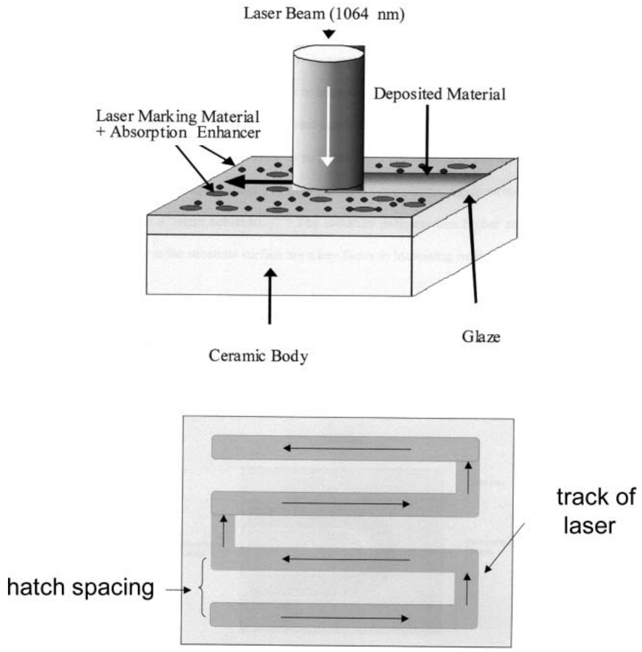


Fig. 5 Schematic diagram of the laser writing process.

Table 2 Optimised conditions for gold deposition

Parameter	XAu(CNR) complexes	$ClAuC(NHPh)[MeN(CH_2CH_2O)_nMe]$ complexes
Medium	ITA 324	Water
% Gold in applied film by weight	15–20	10
Number of passes, power/W, writing speed/cm s^{-1}	4, 5, 25	2, 2, 6 followed by 2, 5, 20
Hatch spacing/cm	0.0001	0.0001
Additives	Aerosil® R7200 (2%)	Aerosil® R7200 (0.5%), Foamex® 842 (0.5%), Epolight® 2340 (2%), Wet 590® (1%)

brightness, adhesion, film thickness, homogeneity of coverage) was maximised through variations in laser parameters, nature and concentration of surfactant and defoamer, concentration of gold precursor and other additives. Parameters for production of the highest quality gold films are given in Table 2.

For the isocyanide complexes, a paste of SiO_2 (Aerosil® R7200, average particle size 12 nm) and XAu(RNC) of appropriate concentration in ITA 324 (a commercially available screen printing medium) was applied to the ceramic substrate using a micrometer adjustable film applicator to give a film of the desired thickness. For the carbene complexes, saturated solutions of the organogold compounds were mixed with SiO_2 (Aerosil® R7200) and Wet® 590 and Foamex® 842 as wetting and antifoaming agents respectively. A water soluble dye Epolight® 2340 absorbing strongly near 1065 nm was added to reduce the proportion of SiO_2 required. In the art of ceramic decoration, SiO_2 is known to reduce the brightness of a gold finish. Samples of the above solution were pipetted into 3 cm^2 moulds placed on the surface of the ceramic material and were allowed to dry to thin films. Several passes of the laser were required to completely eliminate carbonaceous material from the films. Films produced from the isocyanide and carbene precursors are similar in visual quality, giving a burnished gold colour. Control studies on unmarked tiles show that there is no ablation or cracking of the glaze surface on laser treatment. The films pass the European Standard (part 4 of EN12875) for adhesion of domestic ceramics (see Experimental section), FESEM photographs of the films made from XAu(RNC) precursors reveal sub micron sized spherical gold particles (Fig. 6a); similar dispersions of spherical gold particles have previously been reported.[24a–c] The films also exhibit a tracked appearance (Fig. 6b); depending on the thickness of the applied precursor, the thicknesses of the deposited gold films range from a mean height of between 0.69 to 5.06 μm, with corresponding maximum ridge heights of between 2.13 and 14.2 μm. The tracking is probably due to thermo-capillary Marangoni flow of heated (low surface tension) to non-heated (high surface tension) material during passage of the laser.[25a,b]

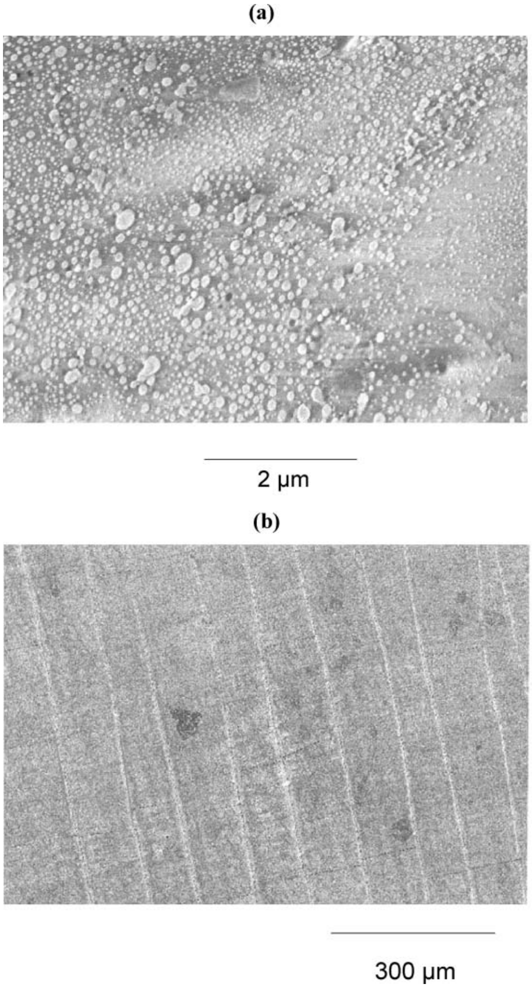


Fig. 6 FESEM photographs of deposited gold.

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