Gold(I) Complexes with Amine Ligands, 4[+]
The Role of N–H···Cl Hydrogen Bonds in Gold(I) Complexes with Aliphatic Amine Ligands

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Various gold(I) complexes of aliphatic amines have been prepared by the reaction of chloro(tetrahydrothiophene)-gold(I) with the respective amines. The stability of these complexes can be attributed partly to the formation of hydrogen bonds involving the N–H functions, and partly to aurophilic interactions. Analysis of these secondary contacts suggests an inverse correlation between lengths of aurophilic interactions and hydrogen bonds.

Introduction

Amine complexes of gold(I) have been little studied and are generally regarded as relatively unstable; this has been rationalized in terms of incompatibility of the soft metal centre with the hard nitrogen donor. Exceptions are furnished by complexes also involving a phosphane or similar ligand as a stabilising influence.[1] From previous studies of systems with solely amine or halide ligands only three structure types are known: (i) $[L_2Au^+][AuCl_2^-]$ (e.g. L = pyridine, 3-methylpyridine),[2][3] (ii) $[L_2Au^+]Cl^-$ (e.g. L = 4-hydroxymethyl-1,5-dimethylimidazole),[4] (iii) [LAuCl] (e.g. L = 2-methylpyridine, piperidine).[3][5] For the imine L = diphenylmethanimine, structures of type (i) and (iii) are known.[6] Type (ii) is also represented by the ammine complex $[(NH_3)_2Au^+]Br^-$.[7]

We have begun a more systematic study of gold(I) complexes with aliphatic amine ligands, generally bearing an N−H function, and have recently reported the structure of $[(\text{pyrrolidine})_4Au_3Cl_3]$,[8] where structure types (ii) and (iii) were present in the same crystal.

Stabilising influences in gold(I) complexes tend to be provided by formally non-bonding Au···Au contacts (aurophilic interactions);[9] the role of hydrogen bonds is of course limited to those systems where suitable functional groups are available, but they have been shown to stabilise e.g. iminegold(I) complexes.[10] In $[(\text{pyrrolidine})_4Au_3Cl_3]$ the Au···Au contacts were long and thus presumably weak [3.2041(7), 3.5834(4) Å],[8] whereas hydrogen bonds were more significant [N···Cl 3.179(6), 3.284(6) Å]. In [(piperidine)AuCl][5] similar Au···Au contacts were observed [Au···Au 3.301(5) Å], but hydrogen bonding was not commented upon, although it is in fact present in the form of bifurcated three-centre hydrogen bonds (Figure 1; N···Cl 3.346, 3.358 Å).

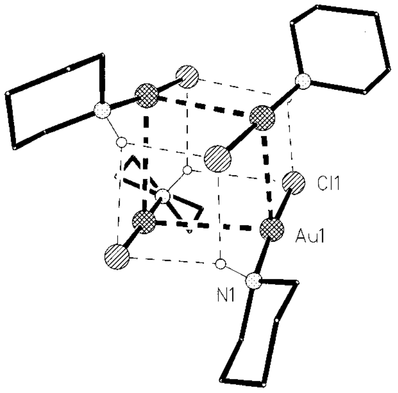

Figure 1. Chloro(piperidine)gold(I),[5] monomeric units related by a $\bar{4}$ axis; only the asymmetric unit is numbered; atom radii are arbitrary; dashed lines represent hydrogen bonds (thin) and aurophilic interactions (thick); carbon-bound hydrogen atoms are omitted for clarity

Here we report the synthesis of gold(I) complexes with the amine ligands piperidine {the complexes [(piperidine)AuCl], $[(\text{piperidine})_2Au^+]Cl^-$, and $[(\text{piperidine})_2Au^+]PF_6^-$ had been previously synthesised by us},[5] 2,2,6,6-tetramethylpiperidine, 4-methylpiperidine, morpholine, piperazine, pyrrolidine, diethylamine, dicyclohexylamine, cyclohexylamine, benzylamine, 1-phenylethylamine, and 3-iodobenzylamine; all complexes were obtained from (tht)AuCl (tht = tetrahydrothiophene) and the corresponding amine. With pyrrolidine, morpholine, cyclohexylamine, and benzylamine, complexes of empirical formula L_2AuCl were obtained; with the other ligands complexes of empirical formula LAuCl. For L = piperidine formerly only crystals of the loosely associated tetramer $(LAuCl)_4$ were obtained;[5] in contrast, we have only been able to obtain crystals of the ionic type $[L_2Au^+]Cl^-$. For L = pyrrolidine, we have now shown that the previously reported $L_4Au_3Cl_3$[8] is a by-product; the main product is $[L_2Au^+]Cl^-$.

No evidence was found for an ionic nature of the complexes in solution: all complexes behave as non-conductors

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in acetone solution (Λ_c < 25 cm^2 Ω^{-1} mol^{-1}; c.f. Λ_c = 140 cm^2 Ω^{-1} mol^{-1} in the case of 1:1 electrolytes such as PPN^+Cl^-), implying that for all aminegold(I) complexes the molecular structure LAuCl is the more stable in solution. Even complexes L_2AuCl were essentially non-conducting, implying some equilibrium involving the uncharged species [LAuCl] in solution.

We have crystallographically characterised complexes of empirical formula LAuCl (L = 2,2,6,6-tetramethylpiperidine: **1**; dicyclohexylamine: **2**), both molecular in nature, and L_2AuCl (L = piperidine: **3**; pyrrolidine: **4**; and cyclohexylamine: **5**). For the latter complexes the ionic structure type (i), $[L_2Au^+]Cl^-$, was found for all three structures. Because no structure is known of a molecular aminegold(I) complex with empirical formula L_2AuX (i.e. where gold would be three-coordinate, with two amine ligands L), we assume an ionic composition for all aminegold(I) complexes of this empirical formula.

Because both types of structure, [LAuCl] and $[L_2Au^+]Cl^-$, have been observed for L = piperidine, it might be concluded that the energetic difference between both types cannot be large. Similar conclusions were drawn from the reactions of (tht)AuCl with methylpyridines,[3] and from ab initio calculations for various spatial associations of complexes with formula $[L_2Au^+][AuCl_2^-]$.[11]

Treatment of the new gold(I) complexes [LAuCl] (L = dicyclohexylamine) or $[L_2Au^+]Cl^-$ (L = piperidine or cyclohexylamine) with $AgSbF_6$ and excess L led in all cases to ionic complexes $[L_2Au^+]SbF_6^-$ (**13**, **14**, and **15**). Complex **13** was crystallographically characterised.

In all the new complexes hydrogen bonding is important in the solid state (Table 1), and for the ionic compounds appears more important than aurophilic interactions (see below). All complexes are less stable in solution than in the solid state. This could be attributed to a change in hydrogen bonding in solution, where the N−H protons are involved in hydrogen bonds to solvent molecules (in ^{1}H-NMR experiments broad signals for the N−H protons were observed, but no variation for the chemical shift). The low solubility of complexes with NH_2 functional groups could also be attributed to hydrogen bonding.

Molecular Structures

We have reported the structure of **2** in a preliminary communication.[12] The structure of **1** (Figure 2) is similar to that of **2** (Figure 3). Both complexes crystallise as loose molecular dimers $(LAuCl)_2$ and display ring motifs. In **1** and **2** only one crystallographically independent hydrogen bond is present, and therefore the ring motifs can be described by the graph set[13] $N_1 = R_2^2(8)$ at unitary level.

The dimers in **1** and **2** have inversion symmetry, making the N−Au−Cl axes antiparallel. Additionally, the molecule of **1** has crystallographic mirror symmetry, with N, Au, Cl, and C3 in the mirror plane. The gold atom in **1** is linearly coordinated [N−Au−Cl 177.21(9)°]. The Au−N and Au−Cl bond lengths of 2.088(3) and 2.2693(10) Å are longer than those in (piperidine)AuCl [2.068(18), 2.256(8) Å][5] but similar to those in **2** [2.077(7), 2.266(2) Å]. The dimers of **1** display aurophilic interaction and hydrogen bonding [Table 1; Au···Au 3.2792(4), N···Cl 3.417(3) Å], comparable to those in **2** [3.2676(14), 3.391(8) Å] and (piperidine)AuCl [3.301(5), 3.346 and 3.580 Å].[5]

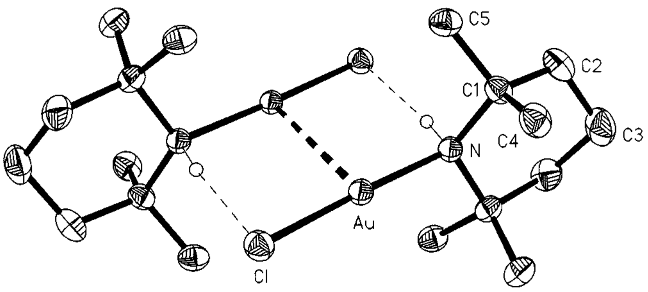

Figure 2. Chloro(2,2,6,6-tetramethylpiperidine)gold(I), **1**, monomeric units related by inversion symmetry; only the asymmetric unit is numbered; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds (thin) and aurophilic interactions (thick); carbon-bound hydrogen atoms are omitted for clarity

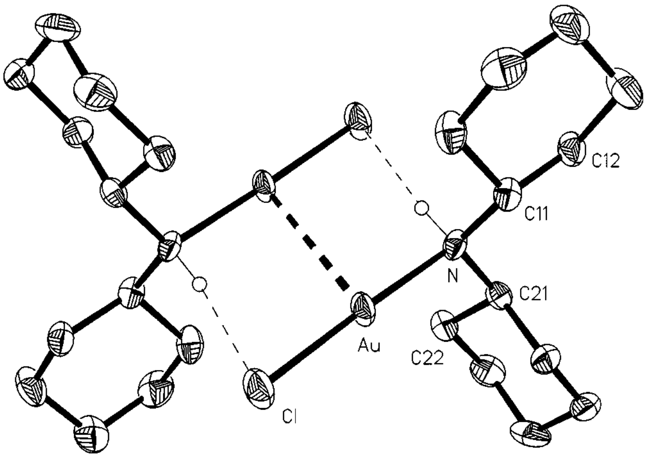

Figure 3. Chloro(dicyclohexylamine)gold(I), **2**, monomeric units related by inversion symmetry; only the asymmetric unit is numbered; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds (thin) and aurophilic interactions (thick); carbon-bound hydrogen atoms are omitted for clarity

Ionic Structures

We have reported the structure of **3** in a preliminary communication.[12] In **3** two crystallographically independent hydrogen bonds are involved in the ring motif (Table 1, Figure 4), which can be described by the graph set $N_2 = R_4^2(12)$ at binary level. In **3** the gold atom is linearly coordinated [N1−Au−N2 179.0(3)°]. The N−Au bond lengths of 2.050(6) and 2.055(6) Å are similar to those of 2.068(18) in (piperidine)AuCl.[5] Thus it can be assumed that the *trans* influence of amine and chloro groups is similar.

The hydrogen bonds (Table 1) in the ionic compound **3** are shorter [N···Cl 3.108(6), 3.122(7) Å] and the Au···Au distance in **3** of 4.085(2) Å is remarkably longer than in

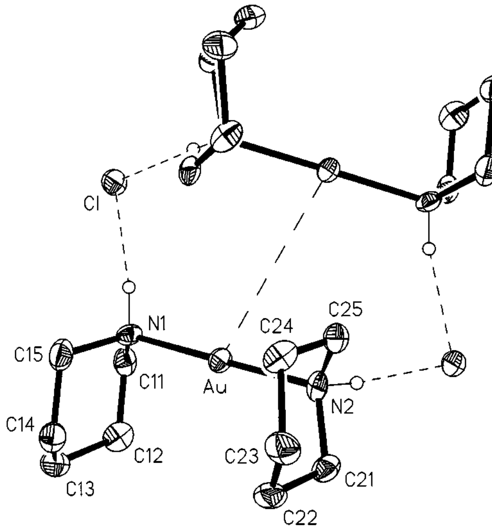

Figure 4. Bis(piperidine)gold(I) chloride, **3**, monomeric units related by a twofold axis; only the asymmetric unit is numbered; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds and aurophilic interactions; carbon-bound hydrogen atoms are omitted for clarity

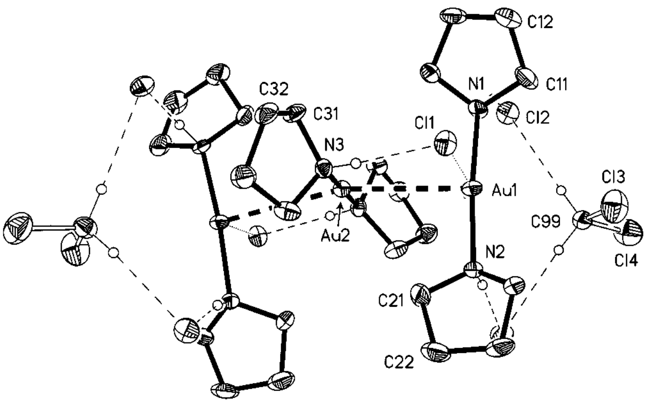

Figure 5. Bis(pyrrolidine)gold(I) chloride (dichloromethane solvate), **4**; only the asymmetric unit is numbered; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds (thin) and aurophilic interactions (thick), dotted lines Au···Cl interactions; carbon-bound hydrogen atoms are omitted for clarity

(piperidine)AuCl,[5] **1** and **2**. Gold−gold distances within the range of 2.50 to 4.00 Å have been considered as aurophilic interactions.[14] Thus the gold-gold interaction in **3** must be extremely weak.

Compounds **4** and **5** both crystallise as dichloromethane solvates $[(L_2AuCl)_3 \cdot (CH_2Cl_2)_2]$ with chain and layer structures. In **4** the L_2Au^+ cations (with L = pyrrolidine) form trimers about a twofold axis, with Au2 on this axis and Cl1 on an inversion centre (Figure 5). Both gold atoms of the asymmetric unit are linearly coordinated [N−Au−N 175.0(3), 179.6(4)°]. The Au−N bond lengths Au1−N1 of 2.055(7), Au1−N2 of 2.052(6), and Au2−N3 of 2.052(5) Å are slightly longer than those in $(pyrrolidine)_4Au_3Cl_3$ of 2.042(6) and 2.048(6) Å.[8] The gold atoms of the trimers in **4** display aurophilic interactions [Au1···Au2 3.2790(7) Å]. The N−Au−N axes within these dimers are nearly perpendicular to each other, with torsion angles of 87.3(3) and −93.2(3)° (N1−Au1···Au2−N3, N2−Au1···Au2−N3, respectively). The hydrogen atom at N3 is involved in a hydrogen bond to Cl1 [N3···Cl1 3.311(5) Å; Table 1]. This hydrogen bond connects the trimers to form chains parallel to (0 0 1) [descriptor $C^1_2(6)$; Figure 6], which are additionally stabilised by short Au···Cl contacts [Au1···Cl1 3.176(1) Å]. The hydrogen atoms at N1 and N2 are involved in hydrogen bonds to Cl2 [N1···Cl2 3.149(7), N2···Cl2′ 3186(7) Å; Table 1]. These hydrogen bonds connect the chains to form layers perpendicular to (0 0 1), with descriptor $C^1_2(6)$ at binary level (Figure 7). The dichloromethane molecules lie within these layers. They show non-conventional hydrogen bonding to the chloride anion Cl2 [C···Cl 3.625 Å (mean)]. One of the chlorine atoms of the dichloromethane molecules is involved in a weak contact to one of the gold atoms [Au1···Cl3 3.635(3) Å], the other chlorine atom displays a Cl···Cl contact to the symmetry-equivalent atom of the next dichloromethane moiety [Cl4···Cl4′ 3.547(5) Å; operator $1 - x$, $1 - y$, $-z$]. The secondary contacts of the dichloromethane molecules result in a honeycomb-like pattern within the layers perpendicular to (0 0 1) (Figure 7). These contacts presumably have a stabilising influence on

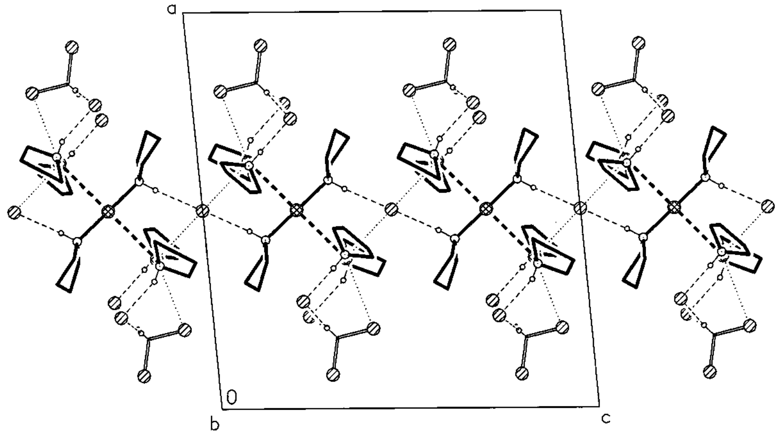

Figure 6. Bis(pyrrolidine)gold(I) chloride (dichloromethane solvate), **4**, chain structure parallel to (0 0 1); atom radii are arbitrary; dashed lines represent hydrogen bonds (thin) and aurophilic interactions (thick), dotted lines Au···Cl interactions; carbon-bound hydrogen atoms, except for CH_2Cl_2, are omitted for clarity

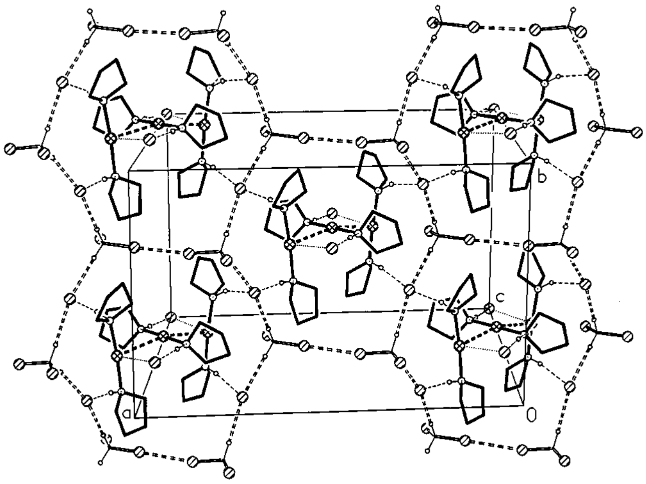

Figure 7. Bis(pyrrolidine)gold(I) chloride (dichloromethane solvate), **4**, layer structure perpendicular to (0 0 1); atom radii are arbitrary; dashed lines represent hydrogen bonds (thin) and aurophilic interactions (thick), dotted lines Au···Cl$^-$ interactions; Au···dichloromethane interactions are not shown; double dashed lines represent secondary interactions of the dichloromethane molecules; carbon-bound hydrogen atoms, except for CH_2Cl_2, are omitted for clarity.

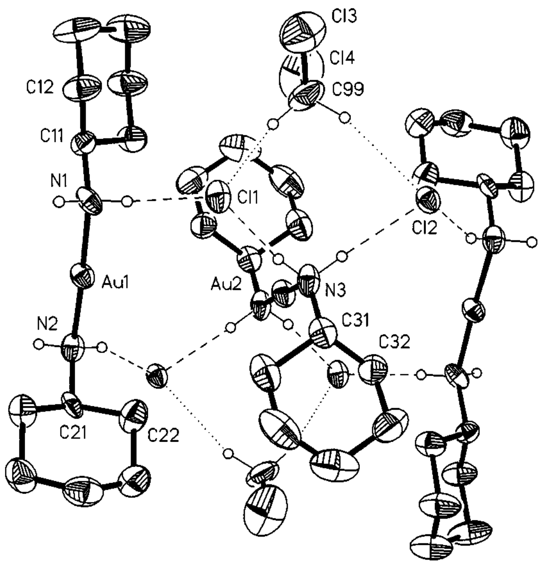

Figure 8. Bis(cyclohexylamine)gold(I) chloride (dichloromethane solvate), **5**, asymmetric unit with numbering scheme; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent N−H hydrogen bonds, dotted lines C−H hydrogen bonds; carbon-bound hydrogen atoms, except for CH_2Cl_2, are omitted for clarity

the structure, in addition to that of the N−H···Cl hydrogen bonds discussed above.

In **5** the L_2Au^+ cations (with L = cyclohexylamine) also form trimeric units (Figure 8), here with inversion symmetry (Au2 and Cl2 lie on inversion centres). The gold atoms are linearly coordinated [N1−Au1−N2 177.6(4), N3−Au2−N3′ 180° (by symmetry)]. The Au−N bond lengths Au1−N1 of 2.036(9), Au1−N2 of 2.047(9) and Au2−N3 of 2.051(8) Å are similar to those in (pyrrolidine)$_4$Au$_3$Cl$_3$ or **2** [2.042(6)−2.055(7) Å].[8] No aurophilic interactions are observed, the shortest Au···Au distance being 4.740(1) Å. The cations are connected to form layers parallel to the *xy* plane via N−H···Cl hydrogen bonds (Figure 9, Table 1), with N···Cl contacts between 3.230(9) and 3.343(9) Å, resulting in a pattern of ring motifs. These rings are associated with descriptors from graph sets at higher levels: $R_4^2(8)$ (binary and ternary), $R_4^2(12)$ (ternary). Every dichloromethane molecule is involved in two non-conventional hydrogen bonds [C99···Cl1 3.576(15), C99···Cl2 3.641(13) Å]. Cl1 is the acceptor atom for one, Cl2 (because of the inversion centre) for two of these hydrogen bonds. The dichloromethane molecules are thus positioned alternately above and below the layer (Figure 8).

Anion Exchange

By preparing the compound bis(dicyclohexylamine)gold(I) hexafluoroantimonate, **13** (Figure 10), it was shown that it is possible to obtain L_2Au^+ cations even with this bulky ligand.

The gold atom in **13** is linearly coordinated [N1−Au−N2 179.1(2)°]. The Au−N bond lengths of 2.085(6) and 2.069(6) Å are similar to those in **2** [2.077(7) Å], consistent

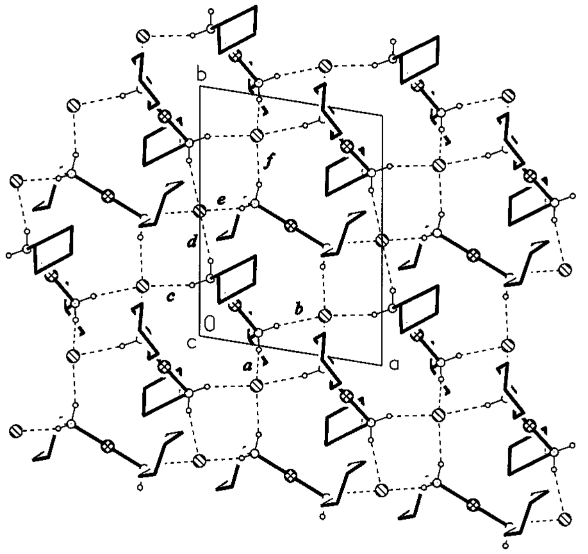

Figure 9. Bis(cyclohexylamine)gold(I) chloride (dichloromethane solvate), **5**, layer structure; atom radii are arbitrary; dashed lines represent hydrogen bonds (Table 1); dichloromethane molecules and carbon-bound hydrogen atoms are omitted for clarity

with our previous observation on *trans* influences (see above). The hydrogen atoms of the amine groups are involved in long hydrogen bonds to fluorine atoms of two hexafluoroantimonate anions [N···F 2.975(8), 3.268(9) Å; Table 1], thereby forming chains [graph set $N_2 = C_2^2(8)$].

Conclusions

Many complexes of gold(I) with aliphatic amines are stable, in contrast to the generally held view based on the

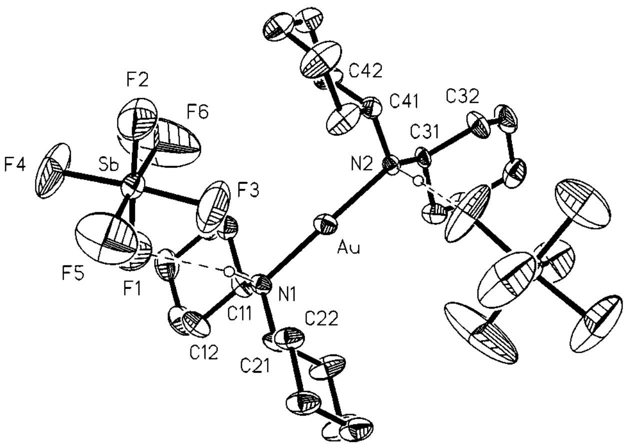

Figure 10. Bis(cyclohexylamine)gold(I) hexafluoroantimonate, **13**, asymmetric unit with numbering scheme; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds

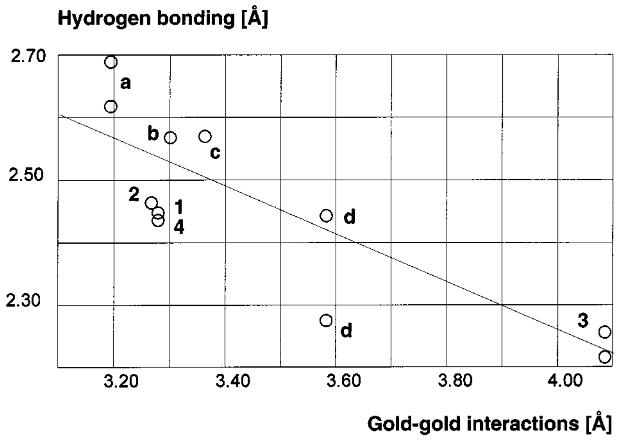

Figure 11. Plot of hydrogen bonding against aurophilic interactions for aminegold(I) complexes; the correlation coefficient is −0.842; a: $[(Ph_2C{=}NH)_2Au^+][AuCl_2^-]$;[6] b: [(piperidine)AuCl];[5] c: $[(Ph_2C{=}NH)AuCl]$;[6] d: $[(pyrrolidine)_4Au_3Cl_3]$[8]

incompatibility of hard ligands with soft metal centres. The stability results in part from the formation of hydrogen bonds involving the N−H functions. In ionic complexes of empirical formula L_2AuCl, hydrogen bonds appear to be more important than in complexes of empirical formula LAuCl; this may be attributable to the positive charge of the gold moiety in the former. Aurophilic interactions appear to have greater influence in complexes of empirical formula LAuCl. By combining data for similar structures (obtained from a search in the CSD database)[15] with our results, we found a tendency that shorter hydrogen bonds are accompanied by longer aurophilic interactions and vice versa (Figure 11). In the complexes with L = pyrrolidine ($L_4Au_3Cl_3$,[8] **4**) hydrogen bonds and aurophilic interactions appear to be necessary to stabilise the complexes, which, surprisingly for complexes with charged gold moieties, display short aurophilic interactions.

Previous difficulties in preparing aminegold(I) complexes may have been caused by (i) the insolubility of many products, (ii) the tendency to form mixtures of complexes (e.g. for pyrrolidine) and/or by-products such as amine hydrochlorides or hemihydrochlorides[16] or (iii) the use of unsuitable amines (e.g. tertiary amines, where we could not obtain stable complexes, presumably because of the lack of hydrogen bonding).

Anions with more functional groups for hydrogen bonding (e.g. disulfonylamine anions) are expected to render a stabilising contribution to aminegold(I) complexes. It may

Table 1. Hydrogen bonds and unitary graph sets (N_1)

Compound	Bond	H···A [Å][a]	H···A [Å][b]	D···A [Å][c]	D-H···A [°]	N_1
1	N−H···Cl^{ii}	2.45(5)	2.40	3.417(3)	174(4)	$R_2^2(8)$
2	N−H···Cl^{vi}	2.46(4)	2.39	3.391(8)	167(8)	$R_2^2(8)$
3	N1−H1···Cl1	2.26(4)	2.16	3.122(7)	158(7)	D
3	N2−H2···Cl1^{i}	2.21(3)	2.10	3.108(6)	172(9)	D
4	N1−H1···Cl2	2.35(7)	2.24	3.149(7)	149(9)	D
4	N2−H2···Cl2^{iii}	2.32(5)	2.18	3.186(7)	171(7)	D
4	N3−H3···Cl1	2.44(4)	2.29	3.311(5)	175(5)	$C_2^1(6)$
4	C99−H99A···Cl2^{iv}	2.63	2.55	3.625(9)	179	D
4	C99−H99B···Cl2^{v}	2.64	2.55	3.625(8)	174	D
5	N1−H1A···Cl1^{vii} *(a)*	2.36	2.26	3.256(9)	166	D
5	N1−H1B···Cl1 *(b)*	2.35	2.25	3.264(10)	171	D
5	N2−H2A···Cl1^{viii} (c)	2.45	2.36	3.297(9)	154	D
5	N2−H2B···Cl2^{viii} *(d)*	2.47	2.37	3.343(9)	159	$D_2^1(3)$
5	N3−H3A···Cl2 *(e)*	2.34	2.25	3.230(9)	161	$C_2^1(6)$
5	N3−H3B···Cl1 *(f)*	2.34	2.25	3.241(9)	165	$D_2^2(7)$
5	C99−H99A···Cl1	2.73	2.66	3.576(15)	144	D
5	C99−H99B···Cl2	2.69	2.60	3.641(13)	162	$D_2^1(3)$
13	N1−H1···F1	2.37	2.28	3.268(9)	163	D
13	N2−H2···F4^{ix}	2.06	1.97	2.975(8)	168	D

[a] Hydrogen bonds without standard deviation were included using a riding model. − [b] Distances were normalised with C−H 1.08, N−H 1.02 Å.[18] − [c] Cf. van der Waals radii: N 1.55, Cl 1.75, H 1.20, C 1.70, F 1.47 Å.[19] − Operators: i: 2 − *x*, *y*, 1.5 − *z*; ii: 1 − *x*, 1 − *y*, 1 − *z*; iii: 1.5 − *x*, 0.5+*y*, 0.5 − *z*; iv: *x* − 0.5, *y* − 0.5, *z*; v: 1 − *x*, *y*, 0.5 − *z*; vi: −*x*, 1 − *y*, 1 − *z*; vii: 1 − *x*, *y*, 1 − *z*; viii: 1+*x*, *y*, *z*; ix: *x* − 0.5, 1.5 − *y*, *z* − 0.5.

Table 2. Crystallographic data

Compound	**1**	**2**	**3**	**4**	**5**	**13**
Formula	$C_9H_{19}AuClN$	$C_{12}H_{23}AuClN$	$C_{10}H_{22}AuClN_2$	$C_{8.67}H_{19.33}AuCl_{2.33}N_2$	$C_{12.67}H_{27.33}AuCl_{2.33}N_2$	$C_{24}H_{46}AuF_6N_2Sb$
M_r	373.67	413.73	402.71	431.28	487.38	795.34
Crystal habit	Colourless tablet	Colourless prism	Colourless prism	Colourless prism	Colourless plate	Colourless prism
Crystal size [mm]	0.30 × 0.10 × 0.08	0.36 × 0.19 × 0.11	0.20 × 0.15 × 0.11	0.20 × 0.20 × 0.10	0.70 × 0.10 × 0.02	0.54 × 0.27 × 0.19
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*Pnnm*	$P\bar{1}$	*C*2/*c*	*C*2/*c*	$P\bar{1}$	$P2_1/n$
Cell dimensions						
a [Å]	10.6298(10)	8.306(3)	21.346(5)	18.859(3)	9.2497(12)	9.880(2)
b [Å]	10.2047(10)	8.978(2)	6.480(2)	11.963(2)	12.0358(15)	19.208(4)
c [Å]	10.5774(10)	10.132(3)	19.630(5)	17.890(2)	12.2298(16)	15.402(4)
α [°]	90	68.24(2)	90	90	100.042(9)	90
β [°]	90	85.17(3)	111.54(3)	95.45(2)	108.767(11)	98.40(2)
γ [°]	90	77.71(3)	90	90	95.455(13)	90
V [Å^3]	1147.37(19)	685.7(3)	2525.8(13)	4018.0(10)	1355.0(3)	2891.6(11)
Z	4	2	8	12	3	4
D_x [Mg m^{-3}]	2.163	2.004	2.118	2.139	1.792	1.827
μ [mm^{-1}]	13.008	10.894	11.829	11.418	8.476	6.055
F(000)	2448	396	1536	704	708	1552
T [°C]	−100	−100	−130	−100	−100	−130
$2\theta_{max}$ [°]	50	50	50	56.6	50	50
Transmission	0.34−0.99	0.65−0.94	0.53−0.68	0.54−1.00	0.59−0.98	0.61−0.97
No. of reflections						
Measured	3720	2402	3568	7330	4604	5837
Independent	3532	2336	2228	1506	4566	5076
R_{int}	0.045	0.039	0.036	0.030	0.023	0.028
Parameters	203	139	135	67	247	307
Restraints	33	1	2	0	45	263
*wR*2(F^2, all refl.)	0.051	0.088	0.067	0.034	0.110	0.108
*R*1[$F>2\sigma(F)$]	0.031	0.036	0.030	0.017	0.046	0.044
S	0.834	0.989	1.053	1.105	0.895	1.016
Max. Δ.σ	0.002	< 0.001	< 0.001	0.002	0.001	< 0.001
Max. Δρ [eÅ^{-3}]	1.143	3.322	1.178	0.762	1.903	2.172

Table 3. Selected bond lengths and angles [Å,°] for **1**

Au−N	2.088(3)	Au−Cl	2.2693(10)
Au−Au^{ii}	3.2792(4)	N−C(1)	1.528(3)
N−Au−Cl	177.21(9)	N−Au−Au^{ii}	82.30(9)
Cl−Au−Au^{ii}	100.49(3)	C(1)^x−N−C(1)	118.9(3)
C(1)−N−Au	112.25(16)		

Operators: ii: 1 − *x*, 1 − *y*, 1 − *z*; x: *x*, *y*, 1 − *z*.

Table 4. Selected bond lengths and angles [Å,°] for **2**

Au−N	2.077(7)	Au−Cl	2.266(2)
Au−Au^{vi}	3.2676(14)	N−C(11)	1.505(11)
N−C(21)	1.505(11)		
N−Au−Cl	177.7(2)	N−Au−Au^{vi}	80.8(2)
Cl−Au−Au^{vi}	101.50(7)	C(11)−N−C(21)	115.1(6)
C(11)−N−Au	113.4(5)	C(21)−N−Au	111.1(5)

Operator: vi: −*x*, 1−*y*, 1−*z*.

be possible to stabilise the less robust amine complexes such as **7** and $[(RNH_2)_2Au^+]$ (R = Me, Et, *t*Bu)[7] with such counter-ions. This influence will be discussed in a forthcoming paper of this series.

Table 5. Selected bond lengths and angles [Å,°] for **3**

Au−N(1)	2.050(6)	Au−N(2)	2.055(6)
N(1)−C(11)	1.493(10)	N(1)−C(15)	1.521(10)
N(2)−C(21)	1.483(10)	N(2)−C(25)	1.502(10)
N(1)−Au−N(2)	179.0(3)	C(11)−N(1)−C(15)	109.9(6)
C(11)−N(1)−Au	116.0(5)	C(15)−N(1)−Au	111.4(5)
C(21)−N(2)−C(25)	110.3(6)	C(21)−N(2)−Au	114.2(5)
C(25)−N(2)−Au	113.5(5)		

Table 6. Selected bond lengths and angles [Å,°] for **4**

Au(1)−N(2)	2.052(6)	Au(1)−N(1)	2.055(7)
Au(1)−Au(2)	3.2790(7)	N(1)−C(14)	1.492(10)
N(1)−C(11)	1.516(9)	N(2)−C(21)	1.466(10)
N(2)−C(24)	1.485(9)	Au(2)−N(3)	2.052(5)
Au(2)−Au(1)^v	3.2790(7)	N(3)−C(31)	1.485(9)
N(3)−C(34)	1.508(9)	C(99)−Cl(3)	1.755(7)
C(99)−Cl(4)	1.761(8)		
N(2)−Au(1)−N(1)	175.0(3)	N(2)−Au(1)−Au(2)	93.49(19)
N(1)−Au(1)−Au(2)	91.49(17)	C(14)−N(1)−C(11)	104.4(6)
C(14)−N(1)−Au(1)	116.9(5)	C(11)−N(1)−Au(1)	112.6(5)
C(21)−N(2)−C(24)	102.8(6)	C(21)−N(2)−Au(1)	117.7(5)
C(24)−N(2)−Au(1)	115.3(5)	N(3)−Au(2)−N(3)^v	179.6(4)
N(3)−Au(2)−Au(1)^v	91.29(14)	N(3)−Au(2)−Au(1)	88.65(14)
Au(1)^v−Au(2)−Au(1)	164.762(17)	C(31)−N(3)−C(34)	104.9(5)
C(31)−N(3)−Au(2)	115.4(4)	C(34)−N(3)−Au(2)	116.3(4)
Cl(3)−C(99)−Cl(4)	110.6(4)		

Operator: v: 1 − *x*, *y*, 0.5 − *z*.

Table 7. Selected bond lengths and angles [Å,°] for **5**

Au(1)−N(1)	2.036(9)	Au(1)−N(2)	2.048(9)
Au(2)−N(3)	2.051(8)	N(1)−C(11)	1.492(14)
N(2)−C(21)	1.470(14)	N(3)−C(31)	1.459(15)
C(99)−Cl(3)	1.742(15)	C(99)−Cl(4)	1.746(14)
N(1)−Au(1)−N(2)	177.6(4)	N(3)^{ii}−Au(2)−N(3)	180.0
C(11)−N(1)−Au(1)	117.2(7)	C(21)−N(2)−Au(1)	117.3(7)
C(31)−N(3)−Au(2)	119.9(7)	Cl(3)−C(99)−Cl(4)	112.3(8)

Operator ii: $1 - x, 1 - y, 1 - z$.

Table 8. Selected bond lengths and angles [Å,°] for **13**

Au−N(2)	2.070(6)	Au−N(1)	2.085(6)
Au−F(3)	3.460(9)	Au−F(4)^{ix}	3.981(7)
N(1)−C(21)	1.501(10)	N(1)−C(11)	1.502(9)
N(2)−C(31)	1.505(9)	N(2)−C(41)	1.526(9)
N(2)−Au−N(1)	179.1(2)	N(2)−Au−F(3)	111.7(2)
N(1)−Au−F(3)	68.6(2)	N(2)−Au−F(4)^{ix}	46.8(2)
N(1)−Au−F(4)^{ix}	132.5(2)	F(3)−Au−F(4)^{ix}	96.46(18)
C(21)−N(1)−C(11)	115.9(6)	C(21)−N(1)−Au	111.4(5)
C(11)−N(1)−Au	112.0(4)	C(31)−N(2)−C(41)	114.1(6)
C(31)−N(2)−Au	113.5(4)	C(41)−N(2)−Au	111.6(4)
Sb−F(3)−Au	129.6(5)		

Operator: ix: $x - 0.5, 1.5 - y, z - 0.5$.

Experimental Section

General: NMR spectra were measured with a Bruker AC 200 spectrometer in $CDCl_3$ solution with TMS as internal standard (if not otherwise stated). Frequencies: 200.1 MHz (^{1}H), 50.3 MHz (^{13}C). − Mass spectra were recorded with a Finnigan MAT 8430. − Conductivities were measured with a WTW LF 530 (LTA 1 electrode) conductometer. − All reactions were carried out with exclusion of light at room temperature. − All aminegold(I) complexes with liquid amines were prepared as follows: (tht)AuCl (tht = tetrahydrothiophene) (160 mg, 0.5 mmol) was dissolved in neat amine (5 mL). The solution was stirred for 1 h with exclusion of light at room temperature; a white precipitate formed. Light petroleum ether was added and after cooling for 1 h at −18 °C the precipitate was filtered off and recrystallised from dichloromethane/light petroleum ether. Except for **5** (see below) crystals were obtained by diffusion of light petroleum ether into dichloromethane solution. − All complexes with SbF_6^- anions were prepared as follows: [LAuCl] or $[L_2Au^+]Cl^-$ (0.5 mmol) was dissolved in a solution of 5 mL of dichloromethane and 1 mL of amine (L) and $AgSbF_6$ (344 mg, 1 mmol) was added. The suspension was stirred for 1 h with exclusion of light at room temperature. The AgCl precipitate was filtered off through a layer of $MgSO_4$. Light petroleum ether was added to the solution and after cooling overnight at −18 °C colourless, light-sensitive crystals were obtained.

Chloro(2,2,6,6-tetramethypiperidine)gold(I) (1): Yield 53%, dec. >122 °C. − ^{1}H NMR: δ = 1.44 (s, 6 H, CH_3), 1.48 (m, 2 H, β-CH_2), 1.57 (s, 6 H, CH_3), 1.65 (m, 2 H, γ-CH_2), 1.76 (m, 2 H, β-CH_2), 4.6 (br., NH). − ^{13}C NMR: δ = 17.12, (γ-CH_2), 28.14, (CH_3), 37.26, (β-CH_2), 59.27 (α-CH_2) (classified by C-H correlation). − EI MS; *m*/*z* (%): 126 (100) [M − CH_3 − AuCl], 141 (2) [M − AuCl]. − Conductivity: $\Lambda_c = 8$ cm^2 Ω^{-1} mol^{-1}. − $C_9H_{19}AuClN$ (373.68): calcd. C 28.93, H 5.12, N 3.75; found C 28.85, H 5.08, N 3.51.

Chloro(dicyclohexylamine)gold(I) (2): Yield 75%, dec. > 114 °C. − ^{1}H NMR: δ = 1.26−1.84 (16 H, CH_2), 2.12, 2.40 [m, 4 H, 2-, 2′-CH_2 (eq.)], 2.99 (m, 2 H, CH). − ^{13}C NMR: δ = 25.05 (3-C), 35.50 (4-C), 34.82 (2-C), 58.73 (1-C). − EI MS; *m*/*z* (%): 181 (16) [M − Au − Cl]. − $C_{12}H_{23}AuClN$ (413.74): calcd. C 34.84, H 5.60, N 3.39; found C 34.86, H 5.55, N 3.34.

Bis(piperidine)gold(I) Chloride (3): Yield 91%, dec. > 86 °C. − ^{1}H NMR: δ = 1.73 (m, 4 H, β-CH_2), 3.25 (m, 4 H, α-CH_2). − ^{13}C NMR: δ = 23.41 (β-CH_2), 26.52 (γ-CH_2), 53.50 (α-CH_2). − EI MS; *m*/*z* (%): 84 (100) [M − Au − Cl − H]. − Conductivity: Λ_c = 24 cm^2 Ω^{-1} mol^{-1}. − $C_{10}H_{22}AuClN_2$ (402.72): calcd. C 29.82, H 5.51, N 6.96; found C 29.34, H 5.35, N 7.06.

Bis(pyrrolidine)gold(I) Chloride (4): Yield 85%, dec. at room temperature. − ^{1}H NMR: δ = 1.90 (br., 4 H, β-CH_2); 3.00 (br., 2 H), 3.54 (br., 2 H) (α-CH_2). − ^{13}C NMR: δ = 23.62 (β-CH_2); 52.54 (α-CH_2). − FAB MS (pos.); *m*/*z* (%): 72 (100) [K − C_4H_8NAu]$^+$. − $C_8H_{18}AuClN_2 \cdot 0.67\,CH_2Cl_2$ (431.20): calcd. C 24.15, H 4.52, N 6.50; found C 23.95, H 4.67, N 7.05; the elemental analysis is affected by co-crystallised dichloromethane, which could not be removed even after prolonged pumping. − (Pyrrolidine)$_4$Au$_3$Cl$_3$[8] was obtained as a by-product of this reaction.

Bis(cyclohexylamine)gold(I) Chloride (5): Crystals were obtained by diffusion of cyclohexylamine into a solution of (tht)AuCl in dichloromethane. Yield 75%, dec. > 114 °C. − ^{1}H NMR: δ = 1.16 (m, 12 H, CH_2, ax.); 1.77 (m, 10 H, CH_2, eq.); 2.62 (m, 2 H, CH); 4.5 (br., NH_2). − ^{13}C NMR: δ = 26.95 (3-C); 31.06 (4-C); 35.54 (2-C); 55.69 (1-C). − EI MS; *m*/*z* (%): 99 (19) [M − $C_6H_{13}NAuCl$]. − $C_{12}H_{26}AuClN_2$ (430.77): calcd. C 33.46, H 6.08, N 6.50; found C 33.57, H 6.07, N 6.52.

Chloro(4-methylpiperidine)gold(I) (6): Yield 55%, dec. > 67 °C. − ^{1}H NMR: δ = 0.87 (d, 3 H, CH_3), 0.93 (d, 3 H, CH_3), 1.28 (m, 1 H, β-CH_2), 1.45 (br., 1 H, γ-CH), 1.63 (m, 1 H, γ-CH), 1.67 (m, 3 H, β-CH_2), 3.01 (m, 2 H, α-CH_2), 3.36 (m, 1 H, α-CH_2), 3.52 (m, 1 H, α-CH_2), 5.5 (br., NH) (classified by C-H correlation). − ^{13}C NMR: δ = 21.60, 21.65 (CH_3); 29.93, 30.14 (γ-CH); 34.17, 35.26 (β-CH_2); 52.28, 53.72 (α-CH_2) [doubling of signals is due to two conformers (*cis* and *trans*)]. − EI MS; *m*/*z* (%): 98 (100) [M − AuCl − H]. − Conductivity: Λ_c = 21 cm^2 Ω^{-1} mol^{-1}. − $C_6H_{13}AuClN$ (331.60): calcd. C 21.73, H 3.95, N 4.22; found C 23.99, H 4.27, N 4.34.

Bis(morpholine)gold(I) Chloride (7): Yield 76%, dec. > 72 °C. This compound was not stable enough to obtain NMR spectra. − EI MS; *m*/*z* (%): 87 (100) [M − $C_4H_9NOAuCl$]. − Conductivity: Λ_c = 22 cm^2 Ω^{-1} mol^{-1}. − $C_8H_{18}AuClN_2O_2$ (406.66): calcd. C 23.63, H 4.46, N 6.89; found C 23.41, H 4.42, N 7.49.

Chloro(piperazine)gold(I) (8): (tht)AuCl (160 mg, 0.5 mmol) was dissolved in a solution of piperazine in ethanol (10 mL, 50% excess of piperazine). The suspension was stirred for 1 h with exclusion of light at room temperature. Diethyl ether was added and after cooling for 1 h at −18 °C the white precipitate was filtered off and recrystallised from dichloromethane/light petroleum ether. Yield 75%, dec. > 109 °C. − ^{1}H NMR: δ = 2.94 (m, 8 H, CH_2). − EI MS; *m*/*z* (%): 86 (66) [M − AuCl]. − $C_4H_{10}AuClN_2$ (318.56): calcd. C 15.08, H 3.16, N 8.79; found C 15.54, H 3.28, N 8.94. − This compound was not soluble enough to obtain crystals.

Chloro(diethylamine)gold(I) (9): Yield 95%, dec. at room temperature. − ^{1}H NMR: δ = 1.39 (br., 6 H, CH_3), 3.02 (br., 4 H, CH_2), 4.9 (br., NH). − EI MS; *m*/*z* (%): 73 (34) [M − AuCl]. − $C_4H_{11}AuClN$ (305.56): calcd. C 15.72, H 3.63, N 4.58; found C 15.68, H 3.69, N 4.63. − This compound was not stable enough to obtain crystals.

Bis(benzylamine)gold(I) Chloride (10): Yield 82%, dec. > 149 °C. This compound was not soluble enough for NMR measurements.

− EI MS; *m/z* (%): 107 (65) [M − C_7H_9NAuCl]. − $C_{14}H_{18}AuClN_2$ (446.73): calcd. C 37.64, H 4.06, N 6.27; found C 37.91, H 4.05, N 6.33. − This compound was not soluble enough to obtain crystals.

Chloro(1-phenylethylamine)gold(I) (11): Yield 46%, dec. > 123°C. − ^{1}H NMR: δ = 1.38, 1.41 (s, 3 H, CH_3), 4.12 (dd, 1 H, CH), 7.35 (m, 2 H, Ph). − EI MS; *m/z* (%): 106 (100) [M − CH_3 − AuCl], 121 (2) [M − AuCl]). − $C_8H_{11}AuClN$ (353.60): calcd. C 27.17, H 3.14, N 3.96; found C 27.36, H 3.09, N 3.77. − This compound was not soluble enough to obtain crystals.

Chloro(3-iodobenzylamine)gold(I) (12): Yield 49%, dec. > 119°C. − ^{1}H NMR ([D$_6$]DMSO): δ = 3.96 (m, 2 H, CH_2), 7.18 (m, 1 H, *m*-Ph), 7.44 (m, 1 H, *p*-Ph), 7.67 (m, 1 H, o^6-Ph), 7.84 (m, 1 H, o^2-Ph), 5.8 (br., NH_2). − EI MS; *m/z* (%): 106 (100) [M − I − AuCl]), 233 (32) [M − AuCl]). − $C_7H_8AuClNI$ (465.47): calcd. C 18.06, H 1.73, N 3.01, Cl 7.62; found C 17.74, H 1.68, N 2.87, Cl 7.64. − This compound was not soluble enough to obtain crystals.

Bis(dicyclohexylamine)gold(I) Hexafluoroantimonate (13): Yield 59%, dec. > 112°C. − ^{1}H NMR ([D$_6$]acetone): δ = 1.07−2.98 (40 H, CH_2); 3.25 (m, 4 H, CH); 5.3 (br., NH). − FAB MS (pos.); *m/z* (%): 559 (100) [K]$^+$. − $C_{24}H_{46}AuF_6N_2Sb$ (795.35): calcd. C 36.24, H 5.83, N 3.52; found C 36.12, H 5.82, N 3.44.

Bis(piperidine)gold(I) Hexafluoroantimonate (14): Yield 30%, dec. > 173°C. − ^{1}H NMR: δ = 1.75 (m, 6 H, β-, γ-CH_2), 3.24 (m, 4 H, α-CH_2), 4.4 (br., NH). − FAB MS (pos.); *m/z* (%): 86 (18) [K − $C_5H_{10}NAu$]$^+$, 282 (2) [K − $C_5H_{11}N$]$^+$, 367 (100) [K]$^+$. − $C_{10}H_{22}AuF_6N_2Sb$ (603.01): calcd. C 19.92, H 3.68, N 4.65; found C 19.81, H 3.70, N 4.59.

Bis(cyclohexylamine)gold(I) Hexafluoroantimonate (15): Yield 23%, dec. > 74°C. − ^{1}H NMR ([D$_6$]acetone): δ = 1.16−2.28 (20 H, CH_2), 3.81 (m, 2 H, CH), 5.5 (br., NH). − FAB MS (pos.); *m/z* (%): 100 (100) [K − $C_6H_{12}NAu$]$^+$, 395 (42) [K]$^+$. − $C_{12}H_{26}AuF_6N_2Sb \cdot 0.5\ C_6H_{13}N$ (680.65): calcd. C 26.47, H 4.81, N 5.14; found C 27.72, H 5.39, N 5.10; the elemental analysis is affected by co-crystallised excess cyclohexylamine, which could not be removed even after prolonged pumping.

X-ray Structure Determinations: Crystal data: Table 2. − Data collection and reduction: The crystals were mounted in inert oil on a glass fibre. Data were measured using Mo-K_α radiation (λ = 0.71073 Å) with a Stoe STADI4 (**3**, **13**), Siemens P4 diffractometer (**2**, **4**, **5**) or a Siemens Smart area detector (**1**), each fitted with an LT-2 low-temperature attachment. Semi-empirical absorption corrections were based on psi-scans (XEMP) (**2**, **3**, **4**, **5**, **13**) or on multiple scans (SADABS) (**1**). Structures were solved by direct (**2**, **3**) or Patterson (**1**, **4**, **5**, **13**) methods and subjected to full-matrix least-squares refinement on F^2 (program SHELXL-97).[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model except for those bonded to nitrogen atoms in **1**, **2**, **3** and **4**, which were refined "freely", in **1**, **2** and **4** with restrained N−H bond lengths. − Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC-440/051 (**2**, **3**),[12] CCDC-113728 (**1**), CCDC-113729 (**4**), CCDC-113730 (**5**) and CCDC-113731 (**13**). Copies may be obtained without charge from: CCDC, Union Road, Cambridge CB2 1EZ, UK [Fax: internat. + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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