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Synthesis, isomerism and supramolecular chemistry of diphenylmethanimine complexes of the coinage metals

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The reactions of $[AuCl(SMe_2)]$ or $[AuBr(C_4H_8S)]$ with 1 equivalent of diphenylmethanimine led to the formation of the complexes $[AuCl(Ph_2C{=}NH)]$ **1a**, $[Au(Ph_2C{=}NH)_2][AuCl_2]$ **1b** and $[Au(Ph_2C{=}NH)_2][AuBr_2]$ **2**, respectively. Treatment of **1a**, **1b** with KI in the two-phase system dichloromethane–water induced a redox process to give Au^0 and $[Au(Ph_2C{=}NH)_2][I_3]$ **3**. The same result was obtained when AuI and $Ph_2C{=}NH$ were allowed to react under anhydrous and oxygen-free conditions. Copper(I) iodide reacted with an excess of $Ph_2C{=}NH$ with formation of the complex $[CuI(Ph_2C{=}NH)]$ **4**. Bis(diphenylmethanimine) complexes of gold, $[Au(Ph_2C{=}NH)_2]BF_4$ **5**, and silver, $[Ag(Ph_2C{=}NH)_2]BF_4$ **6**, were prepared by the reaction of 2 equivalents of the ketimine and $[Au(PhCN)_2]BF_4$ or $AgBF_4$ in dichloromethane or tetrahydrofuran solutions, respectively. The crystal structures of the complexes **1a**, **1b**, **2**, **3**, **5** and **6** have been determined. The $(Ph_2C{=}NH)AuCl$ units of compound **1a** form infinite zigzag chains *via* weak Au · · · Au contacts [3.3633(5) Å]. In **1b** two $AuCl_2^-$ anions and two $(Ph_2C{=}NH)_2Au^+$ cations form a tetranuclear Z-type unit with Au · · · Au contacts of 3.1944(5) [Au(1) · · · Au(2)], 3.604(1) [Au(1) · · · Au(2′)] and 3.392(1)Å [Au(1) · · · Au(1′)]. The N–H · · · Cl geometry suggests hydrogen bonding between the hydrogen and chlorine atoms of neighbouring ions. The bromine compound **2** is isostructural to the chloride **1b** with slightly longer Au · · · Au distances. Compound **3** shows bis(diphenylmethanimine)gold(I) cations and triiodide anions with no anomalies in the packing and in bond distances and angles. The geometry of the silver(I) and gold(I) complexes **5** and **6** are quite similar except for the observation that the Au–N bond is 0.11 Å shorter than the Ag–N bond, which suggests that two-co-ordinate gold(I) is indeed smaller than two-co-ordinate silver(I) in systems with nitrogen-containing ligands, as previously observed for phosphine complexes.

Aldimines (**A**) and ketimines (**B**) have a long history in organic chemistry as important derivatives of carbonyl compounds. They have been widely used in organic synthesis and for the identification of the parent compounds, *e.g.* in carbohydrate chemistry. Their role as substrates or ligands in inorganic and organometallic chemistry is still only poorly developed, however, except for a certain focus on the complexes of the coinage metals (Cu, Ag and Au).

Previous work in this area arose from the use of copper salts in the oxidative coupling of ammonia to produce hydrazine *via* ketimine intermediates.[1–4] The mechanism proposed for the action of the copper salts in both the stoichiometric and catalytic versions of this reaction included the formation of ketimine complexes (**C**), but none of these intermediates has been isolated and structurally characterized.

Our own recent studies in the co-ordination chemistry of gold(I) with various nitrogen-containing ligands (amines,[5–10] imines,[11] carbodiimines,[12] amides,[13] phosphinimines,[14,15] isocyanides,[16,17] *etc.*) led us to an investigation of the ligand behaviour of aldimines and ketimines. The work initiated in this context was also aimed at an improved understanding of the intriguing supramolecular chemistry of coinage metal compounds in general, and of gold(I) compounds in particular.[18–21] Owing to the open co-ordination sphere at their nitrogen atoms, aldimines and ketimines can be expected to function as excellent donors in mono- and poly-nuclear complexes.

In this account we present our recent results on simple mononuclear complexes of diphenylmethanimine $Ph_2C{=}NH$ as a ligand prototype with gold(I) and silver(I) salts. Unexpected phenomena of isomerism and aggregation made this study a much more interesting endeavour than originally expected.

Preparative Results

(Diphenylmethanimine)gold(I) chloride and its ionic isomer

The reaction of (dimethyl sulfide)gold(I) chloride, $[AuCl(SMe_2)]$, with equimolar quantities of $Ph_2C{=}NH$ gives a colourless product [equation (1)]. This initial product, as well as

$$3[AuCl(SMe_2)] + 3Ph_2C{=}NH \longrightarrow \underset{\mathbf{1a}}{[AuCl(Ph_2C{=}NH)]} + \underset{\mathbf{1b}}{[Au(Ph_2C{=}NH)_2][AuCl_2]} + 3Me_2S \quad (1)$$

the material obtained after recrystallization, consists of roughly equivalent amounts of two different types of crystals, which can be separated under a microscope. The two separate forms have the same analytical composition and are therefore isomers {$[AuCl(Ph_2C{=}NH)]$ **1a**, m.p. 223 °C; $[Au(Ph_2C{=}NH)_2][AuCl_2]$ **1b**, m.p. 227 °C}.

Solutions of the mixture or of one of the components in chloroform give almost identical NMR spectra, suggesting rapid ligand exchange between the isomers. The IR spectra of the crystals are slightly, but distinctly different, however, with ν(N–H) and ν(C=N) stretching vibrations at 3249.9/3205.3 and 1592.0/1598.9 cm^{-1} for **1a** and **1b**, respectively, as representative examples. The data indicate that both compounds contain Au-bonded $Ph_2C{=}NH$, but in different environments. Fast atom bombardment (FAB) mass spectral studies gave a first clue as to the identity of at least one of the isomers in that they showed, amongst others, the cation $[Au(Ph_2C{=}NH)_2]^+$ and the anion $[AuCl_2]^-$, which are proof of the presence of an ionic species with these two components (**1b**). This result was later confirmed in structural studies (below).

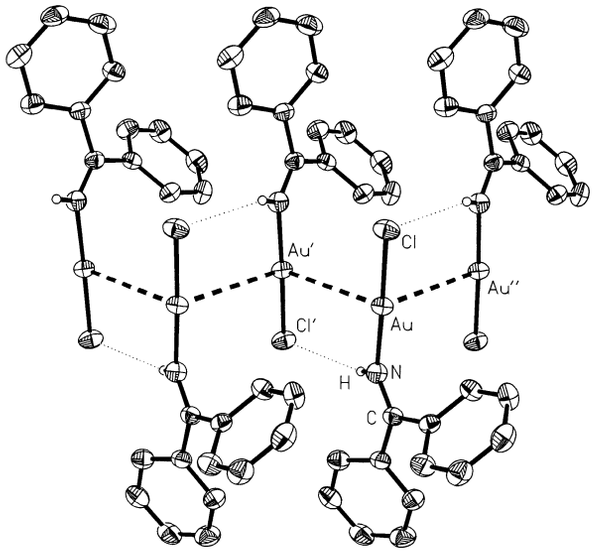

Fig. 1 Infinite zigzag chains in [AuCl(Ph$_2$C=NH)] **1a**, formed *via* weak Au · · · Au interactions and hydrogen bonds, (ORTEP,[23] 50% probability ellipsoids phenyl hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Au · · · Au′ 3.3633(5), Au–N 2.019(6), Au–Cl 2.250(2), N–C 1.269(8), N–H 0.900, Cl′ · · · H 2.570 and N · · · Cl′ 3.470; N–H · · · Cl′ 140.7, N–Au–Cl 176.9(2), N–Au–Au′ 88.8(2), N–Au–Au″ 93.3(2), Au′–Au–Au″ 107.17(2), Cl–Au–Au′ 91.43(5), Cl–Au–Au″ 89.60(4), C–N–Au 129.4(5), C–N–H 115.3(4) and Au–N–H 115.4(2)

Bis(diphenylmethanimine)gold(I) dibromoaurate(I) and triiodide

Treatment of (tetrahydrothiophene)gold(I) bromide, [AuBr(C$_4$H$_8$S)], with 1 equivalent of Ph$_2$C=NH affords a yellow solid product [equation (2)], the IR spectra of which again indicate

$$2[AuBr(C_4H_8S)] + 2Ph_2C{=}NH \longrightarrow [Au(Ph_2C{=}NH)_2][AuBr_2] + C_4H_8S \quad (2)$$

2

the presence of isomers [3230.8/3200.0 and 1585/1572 cm^{-1} for ν(N–H) and ν(C=N), respectively]. Upon recrystallization only one isomer could be obtained in the form of single crystals, which was later identified as the ionic isomer [Au(Ph$_2$C=NH)$_2$][AuBr$_2$] **2**. Crystals of **2** are isomorphous to those of **1b**.

All attempts to prepare a compound of composition [AuI(Ph$_2$C=NH)] (or its ionic counterpart) either from AuI and Ph$_2$C=NH or from **1a** and KI met with failure. In all cases deeply purple solutions were obtained, from which, surprisingly, a triiodide [Au(Ph$_2$C=NH)$_2$][I$_3$] **3** could be crystallized, as confirmed also by X-ray crystallography (below). In all preparative experiments gold metal was produced as easily recognized from a metal mirror at the wall of the reaction vessels, equations (3a) and (3b). The IR spectra of the product confirm

$$3[AuCl(Ph_2C{=}NH)] + 3KI \longrightarrow [Au(Ph_2C{=}NH)_2][I_3] + 2Au + 3KCl \quad (3a)$$

3

$$3AuI + 2Ph_2C{=}NH \longrightarrow [Au(Ph_2C{=}NH)_2][I_3] + 2Au \quad (3b)$$

the presence of only one isomer [*e.g.* 3249.9 and 1588.4 cm^{-1} for ν(N–H) and ν(C=N), respectively]. It appears that the reactions lead to a partial redox process to give gold metal and iodine, the latter being taken up by I$^-$ to form the triiodide. Recent work by Nakao and Sone[22] supports this conclusion. This complication was unexpected since most L–Au–X complexes show a more uniform behaviour for X = Cl, Br or I.

Preliminary experiments with [CuI(Ph$_2$C=NH)] **4** also gave unsatisfactory results. The product was found to be unstable in solution, and the orange crystals produced from the reaction mixture were not satisfactory for an X-ray study.

Bis(diphenylmethanimine)-gold(I) and -silver(I) tetrafluoroborate

Compounds **1b**, **2** and **3** all contain the [Au(Ph$_2$C=NH)$_2$]$^+$ cation, together with the anions [AuCl$_2$]$^-$, [AuBr$_2$]$^-$ and [I$_3$]$^-$, respectively. In order to provide another set of related compounds with 'innocent' counter ions instead of the 'conspicuous' dihalogenogold(I) and triiodide anions, the pair of tetrafluoroborates was prepared for silver(I) and gold(I). The reactions of 2 equivalents of Ph$_2$C=NH with either [Au(PhCN)$_2$]BF$_4$ or AgBF$_4$ give high yields of colourless crystalline materials, which are readily identified as the 2:1 complexes [Au(Ph$_2$C=NH)$_2$]BF$_4$ **5** and [Ag(Ph$_2$C=NH)$_2$]BF$_4$ **6**, equations (4) and (5). The solubility of the compounds is very limited even

$$[Au(PhCN)_2]BF_4 + 2Ph_2C{=}NH \longrightarrow [Au(Ph_2C{=}NH)_2]BF_4 + 2PhCN \quad (4)$$

5

$$AgBF_4 + 2Ph_2C{=}NH \longrightarrow [Ag(Ph_2C{=}NH)_2]BF_4 \quad (5)$$

6

in strongly polar solvents, which affects the quality of NMR data.

Molecular and Supramolecular Structures

The compound [AuCl(Ph$_2$C=NH)] **1a** crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ formula units in the unit cell. The monomeric units are paired up to give centrosymmetric dimers with contacts Au · · · Au′ 3.3633(5) Å, which are aggregated further into corrugated ribbons *via* equivalent contacts [Au · · · Au′, Au″ 3.3633(5) Å] (Fig. 1). The folding of the ribbon is characterized by the angle Au′–Au–Au″ 107.17(2)°. All N–Au–Au′(Au″) and Cl–Au–Au′(Au″) angles are close to 90°.

This assembly is not without precedent in gold chemistry and can be taken as just another example of auriophilicity-determined supramolecular chemistry, albeit with rather weak metal–metal interactions as judged from the rather long Au · · · Au separations. From close inspection of the details it appears, however, that there may be support of the backbone structure from weak N–H · · · Cl′ hydrogen bonds with dimensions N–H 0.900, H · · · Cl′ 2.570, N · · · Cl′ 3.470 Å and N–H · · · Cl′ 140.7°. The Au–N and Au–Cl distances show no anomalies, and the co-ordination at the gold atom is close to linear. The ketimine ligands have a standard geometry.

Crystals of the compounds [Au(Ph$_2$C=NH)$_2$]$^+$[AuX$_2$]$^-$ (X = Cl **1b** or Br **2**) are isomorphous (monoclinic, space group $P2_1/n$, $Z = 4$) and the molecular structures are very similar (Fig. 2). In the present description and discussion of the structures the chloride complex **1b** is considered as a representative example.

Compound **1b** can be described as a tetranuclear unit (four gold atoms) composed of two [AuCl$_2$]$^-$ anions and two [Au(Ph$_2$C=NH)$_2$]$^+$ cations which is structurally based on a parallelogram of gold atoms (with a crystallographic centre of inversion at its centre, Fig. 2). This parallelogram has two short and two large edges [Au(1) · · · Au(2) 3.1944(5), Au(1) · · · Au(2′) 3.604(1) Å] and a transannular contact Au(1) · · · Au(1′) of 3.392(1) Å. If the longest of these metal–metal contacts [Au(1) · · · Au(2′)] is considered too large for gold–gold bonding, the organization of the gold atoms can also be addressed as Z type. Finally, simplifying further, if the medium contact Au(1) · · · Au(1′) is also considered as only very weak, the assembly is an aggregate of two dinuclear units composed of one anion and one cation. It is obvious that the aggregation of the two components arises both from auriophilicity [Au(1) · · · Au(2)] and from N(1)–H(1) · · · Cl(1)/N(2)–H(2) · · · Cl(2) hydro-

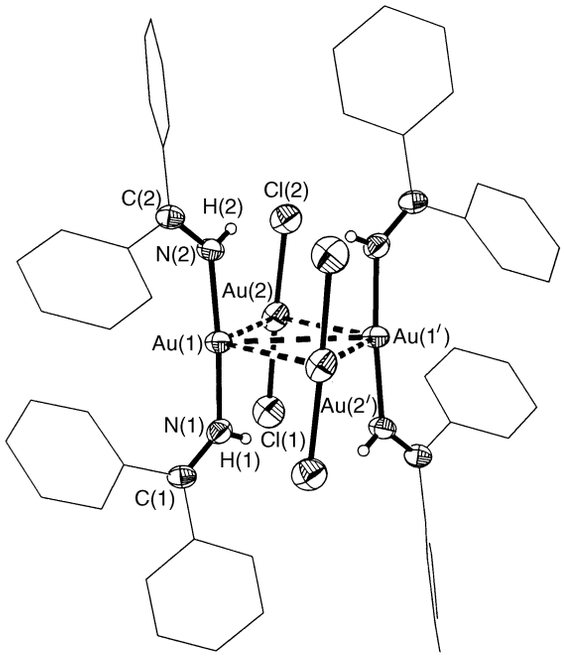

Fig. 2 Tetranuclear unit of $\{[Au(Ph_2C{=}NH)_2][AuCl_2]\}_2$ in compound **1b** (ORTEP, 50% probability ellipsoids, with exception of the phenyl carbon atoms; phenyl hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Au(1)–N(1) 1.995(7), Au(1)–N(2) 2.007(7), Au(1)···Au(2) 3.1944(5), Au(2)–Cl(1) 2.278(3), Au(2)–Cl(2) 2.269(2), N(1)–C(1) 1.291(11), N(2)–C(2) 1.284(10), N(1)–H(1) 0.76(11), N(2)–H(2) 0.75(10), H(1)···Cl(1) 2.620, H(2)···Cl(2) 2.686, N(1)···Cl(1) 3.377 and N(2)···Cl(2) 3.433; N(1)–H(1)···Cl(1) 134.1, N(2)–H(2)···Cl(2) 143.8, N(1)–Au(1)–N(2) 173.3(3), Cl(1)–Au(2)–Cl(2) 175.78(8), N(1)–Au(1)–Au(2) 87.0(2), N(2)–Au(1)–Au(2) 90.3(2), Cl(1)–Au(2)–Au(1) 92.16(6), C(1)–N(1)–Au(1) 130.7(6), Au(1)–N(1)–H(1) 113(8), C(2)–N(2)–Au(1) 130.1(6), Au(1)–N(2)–H(2) 119(8), C(1)–N(1)–H(1) 117(8) and C(2)–N(2)–H(2) 111(8)

gen bonding, as already suggested for the extended structure of **1a** (above).

The configuration of the anions and cations in compound **1b** is quasi-linear at the gold atoms, with two almost equivalent Au–N and Au–Cl distances. It should be noted that these Au–N distances (in a cation) are shorter than in the neutral molecule **1a**, while the Au–Cl distances (in an anion) are longer than in the neutral molecule. Angles N–Au–Au and Cl–Au–Au are all close to rectangular as expected for auriophilic contacts.

The geometry of the bromine analogue **2** follows the same structural principle. There is again a parallelogram of gold atoms in a tetranuclear unit comprising two $[AuBr_2]^-$ anions and two $[Au(Ph_2C{=}NH)_2]^+$ cations. The contacts Au(1)···Au(2), Au(1)···Au(2′) and Au(1)···Au(1′) are 3.268(1), 3.597(1) and 3.552(1) Å long, respectively, suggesting again a Z-type bonding to prevail. The individual cation/anion pair has the shortest Au···Au contact [Au(1)···Au(2)] and its geometry is predestined for hydrogen bonding, albeit this may be weak owing to the larger separation of the N–H and Br components.

Crystals of the compound $[Au(Ph_2C{=}NH)_2]^+I_3^-$ **3** are orthorhombic, space group *Pbcn*, with $Z = 4$ formula units in the unit cell. The lattice contains cations with a crystallographic two-fold axis passing through the gold atom. These cations are chiral, and the enantiomers are related by a centre of inversion, which is located at the central iodine atom of the triiodide anions (Fig. 3). The anion is thus linear by symmetry and has two equivalent I(1)[I(1′)]–I(2) distances. The cations are slightly bent at Au [N–Au–N′ 176.0(2)°] with equal Au–N distances. These data are comparable to those of **1b** and **2** which contain the same cation, but as part of a tetranuclear aggregate. Inspection of Fig. 3 shows that the relative orientation of the ions tempts one to suggest hydrogen bonding between cations and

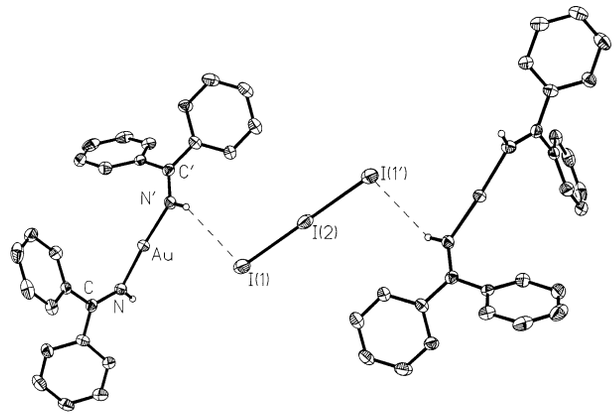

Fig. 3 Crystal structure of $[Au(Ph_2C{=}NH)_2][I_3]$ **3** (ORTEP, 50% probability ellipsoids, phenyl hydrogen atoms omitted). Two bis(diphenylmethanimine)gold(I) cations and one triiodide anion are shown. Selected bond lengths (Å) and angles (°): Au–N 2.011(4), I(1)–I(2) 2.9111(4), N–C 1.290(6), N′–H′ 0.900 and N′···I(1) 3.681; N′–H′–I(1) 131.6, N–Au–N′ 176.0(2), I(1)–I(2)–I(1′) 180.0, C–N–Au 130.4(3), C–N–H 114.7(3) and Au–N–H 114.92(11)

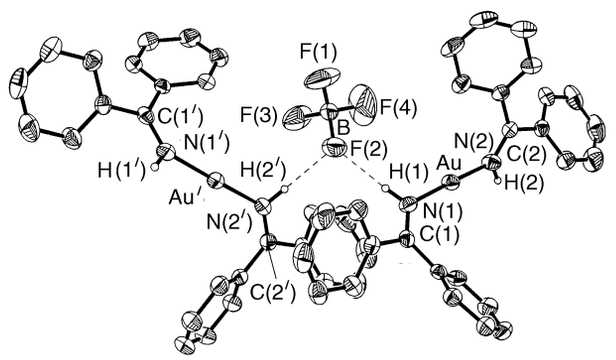

Fig. 4 Crystal structure of $[Au(Ph_2C{=}NH)_2]BF_4{\cdot}CH_2Cl_2$ **5**·CH_2Cl_2 (ORTEP, 50% probability ellipsoids, phenyl hydrogen atoms omitted). Two bis(diphenylmethanimine)gold(I) cations and one tetrafluoroborate anion are shown. Selected bond lengths (Å) and angles (°): Au–N(1) 1.999(4), Au–N(2) 1.998(4), N(1)–C(1) 1.292(5), N(2)–C(2) 1.282(6), B–F(1) 1.335(7), B–F(2) 1.390(6), B–F(3) 1.362(7), B–F(4) 1.307(8), N(1)–H(1) 0.901, F(2)···H(1) 2.112, N(2′)–H(2′) 0.900, H(2′)···F(2) 2.113 and N(2′)···F(2) 3.013; N(1)–H(1)···F(2) 176.1, N(2′)–H(2′)···F(2) 167.6, N(1)–Au–N(2) 178.4(2), C(1)–N(1)–Au 131.8(3), C(2)–N(2)–Au 134.1(3), C(1)–N(1)–H(1) 113.8(2), C(2)–N(2)–H(2) 112.9(3), Au–N(1)–H(1) 114.37(11) and Au–N(2)–H(2) 112.97(10)

anions, but the N–H···I contacts (0.900/3.021 Å) are even longer than in **2** and thus almost prohibitive for discrete interactions.

Crystals of $[Au(Ph_2C{=}NH)_2]^+BF_4^-{\cdot}CH_2Cl_2$ **5**·CH_2Cl_2 are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell. The lattice consists of tetrafluoroborate anions and bis(ketimine)gold(I) cations which have no crystallographically imposed symmetry. The geometry of the cation is close to that of point group C_2, however, and the dimensions are not unusual. The conformation is different from that in compounds **1b**, **2** and **3** in that the two ketimine double bonds can be taken as single-*trans* to each other (Fig. 4), while they were single-*cis* in **1b**, **2** and **3**. The tetrafluoroborate anions are engaged in hydrogen bonding to the N–H groups of the cations, with two contacts (F···H–N) originating from the same fluorine atom [F(2)]. Accordingly, the distance B–F(2) is longer than the remaining three B–F bonds, but standard deviations are large for these data. The N(1)–Au–N(2) unit is linear with two virtually identical Au–N bonds.

Crystals of $[Ag(Ph_2C{=}NH)_2]^+BF_4^-$ **6** are monoclinic, space group *C*2/*c*, with $Z = 4$ formula units in the unit cell. Contrary to the asymmetrical structure of compound **5**, a two-fold axis

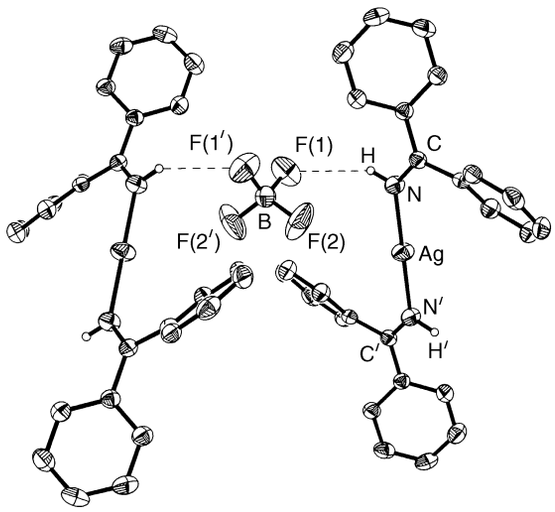

Fig. 5 Crystal structure of $[Ag(Ph_2C{=}NH)_2]BF_4$ **6** (ORTEP, 50% probability ellipsoids, phenyl hydrogen atoms omitted). Two bis(diphenylmethanimine)silver(I) cations and one tetrafluoroborate anion are shown. Selected bond lengths (Å) and angles (°): Ag–N 2.113(2), N–C 1.2793(3), N–H 0.900, B–F(1) 1.382(4), B–F(2) 1.358(3), F(1)···H 2.510 and F(1)···N 3.286; F(1)···H–N 144.7, N′–Ag–N 180.0, C–N–Ag 131.9(2), C–N–H 114.2(2) and Ag–N–H 113.84(6)

passes through the boron atom of the anion in **6**, and the two ligands of the cation (the C=N double bonds of which are in a single-*trans* conformation) are also related by symmetry (Fig. 5). Hydrogen bonding between anions and cations occurs through two of the four fluorine atoms [F(1), F(1′)], but is of the same type as in **5**.

Although taken from entirely different lattices (different space groups, with and without crystal solvent), the cations of compounds **5** and **6** are almost superimposible regarding the general configuration and conformation, except for the different Au/Ag–N bond lengths, which are Ag–N 2.113(2) Å in **6** and Au–N 1.9985 Å (average) in **5**. This result confirms recent findings[24] that the covalent radius of two-co-ordinate Au^I is significantly smaller than the radius of two-co-ordinate Ag^I (by *ca.* 6%).

Conclusion

The present work has shown that ketimines of the type $R_2C{=}NH$ are excellent ligands for salts of the two heavy coinage metals Ag^I and Au^I. For the prototype ligand $Ph_2C{=}NH$ (L) it could be demonstrated that both 1:1 and 2:1 complexes can be obtained. The former can exist as neutral molecules L–Au–X or as ionic isomers $[ML_2]^+[MX_2]^-$ (X = Cl or Br) containing the same cationic units as the 2:1 complexes $[ML_2]^+Y^-$ (Y = BF_4 or I_3).

The structures of the neutral, cationic and anionic units feature linearly two-co-ordinated metal atoms with the ligands fixed to the metals through their planar three-co-ordinated nitrogen atoms. These units can be aggregated to give dimers, tetramers or polymers *via* auriophilic bonding between gold atoms, supported by hydrogen bonding N–H···X, Y.

In the $[AuL_2]^+$ cations the double bonds of the two ligands can be present in single-*trans* or single-*cis* conformations depending on the crystal environment. Comparison of analogous complexes shows conclusively that in the present compounds the covalent radius of gold(I) is smaller than that of silver(I), corroborating recent results for phosphine complexes.[24]

Experimental

All experiments were carried out under an atmosphere of dry, purified nitrogen. Glassware was dried and filled with nitrogen, and solvents were distilled and kept under nitrogen. Instruments: NMR, JEOL GX 400, $SiMe_4$ as internal standard; IR, Perkin-Elmer (type 1600 series FT-IR); mass spectra, Finnigan MAT 90. Microanalyses were performed in-house by combustion and atom absorption spectroscopy. Starting materials were either commercially available or were prepared following literature procedures: $Ph_2C{=}NH$,[25] $[AuCl(SMe_2)]$,[26] $[AuBr(C_4H_8S)]$[27] and $[Au(PhCN)_2]BF_4$.[28]

Preparations

(Diphenylmethanimine)gold(I) chloride 1a, 1b. To a solution of $[AuCl(SMe_2)]$ (0.177 g, 0.60 mmol) in dichloromethane (10 cm^3) was added diphenylmethanimine (101 μl, 0.60 mmol) at room temperature. The solution immediately became pale yellow. After stirring for 3 h the product (0.166 g, 67% yield) was precipitated by adding pentane. The light- and air-stable powder was recrystallized from a dichloromethane–hexane mixture, whereby two different types of crystals were obtained; $[AuCl(Ph_2C{=}NH)]$ **1a**, m.p. 223 °C, and $[Au(Ph_2C{=}NH)_2][AuCl_2]$ **1b**, m.p. 227 °C (Found: C, 37.0; H, 2.9; N, 3.0. $C_{13}H_{11}AuClN$ **1a**/**1b** requires C, 37.7; H, 2.7; N, 3.4%). $\delta_H(CD_3CN)$: 9.74 (1 H, br s, NH) and 8.88–8.45 (10 H, m, Ph). FAB mass spectrum: cations, *m/z* 559, $[Au(Ph_2C{=}NH)_2]^+$, 31%; anions, *m/z* 266.9, $[AuCl_2]^-$, 2.5%.

Bis(diphenylmethanimine)gold(I) dibromoaurate 2. To a solution of $[AuBr(C_4H_8S)]$ (0.215 g, 0.59 mmol) in dichloromethane (15 cm^3) was added $Ph_2C{=}NH$ (99 μl, 0.59 mmol) at room temperature. After 30 min the solvent was removed, the light yellow residue was taken up in dichloromethane and the solution layered with pentane. After 2 d colourless air-stable crystals (0.212 g, 78% yield) were isolated, m.p. 219 °C (Found: C, 34.0; H, 2.3; N, 2.9. $C_{13}H_{11}AuBrN$ requires C, 34.1; H, 2.4; N, 3.1%). $\delta_H(CDCl_3)$: 9.21 (1 H, br s, NH) and 7.90–7.38 (10 H, m, Ph).

Bis(diphenylmethanimine)gold(I) triiodide 3. (*a*) To a solution of compound **1** (0.178 g, 0.43 mmol) in dichloromethane (15 cm^3) was added KI (0.072 g, 0.43 mmol) in water (5 cm^3) at room temperature and the two-phase mixture was stirred. Gold metal (0.057 g) precipitated and the dichloromethane phase became deep red-brown. The water was removed and the dichloromethane phase was washed three times with small portions of water. Then the solvent was removed in a vacuum and the red-brown residue taken up with dry dichloromethane. Upon layering this solution with pentane red-brown crystals (0.102 g, 76% yield) were obtained.

(*b*) To a suspension of AuI (0.108 g, 0.33 mmol) in thf (10 cm^3) was added $Ph_2C{=}NH$ (56 μl, 0.33 mmol). After stirring for 3 h the solution turned to deep red-brown and gold metal (0.032 g) precipitated. The solution was filtered, the thf was removed in a vacuum and the red-brown residue crystallized (0.086 g, 82% yield) (see above). M.p. 162 °C (Found: C, 32.9; H, 2.0; N, 2.7. $C_{26}H_{22}AuI_3N_2$ requires C, 33.2; H, 2.4; N, 3.0%). $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3250s (NH), 1588s (C=N). $\delta_H(CDCl_3)$ 7.55–7.42 (br m, Ph); NH not observed due to low solubility. FAB mass spectrum: cations, *m/z* 182.2, $[Ph_2C{=}NH_2]^+$, 100; 559.4, $[Au(Ph_2C{=}NH)_2]^+$, 2%; anions, *m/z* 450.7, $[AuI_2]^-$, 100; 774.6, $[Au_2I_3]^-$, 4.5%.

(Diphenylmethanimine)copper(I) iodide 4. To a suspension of CuI (0.249 g, 1.31 mmol) in thf (10 cm^3) was added $Ph_2C{=}NH$ (438 μl, 2.61 mmol) in one portion at room temperature. The CuI dissolved and the solution became bright orange and was stirred for 1 h. By layering a reduced volume of this reaction mixture with pentane yellow-orange needles (0.362 g, 74% yield) were obtained, m.p. 144 °C (Found: C, 42.1; H, 3.0; N, 3.7. $C_{13}H_{11}CuIN$ requires C, 42.0; H, 3.0; N, 3.8%). Solutions of the compound in $CHCl_3$ or thf are not stable and some CuI precipitates. Therefore no NMR spectra could be recorded; $\tilde{\nu}_{max}$(KBr)/cm^{-1} 3288s (NH) and 1590s (C=N).

Table 1 Crystallographic data for [AuCl(Ph_2C=NH)] **1a**, [Au(Ph_2C=$NH)_2$][$AuCl_2$] **1b**, [Au(Ph_2C=$NH)_2$][$AuBr_2$] **2**, [Au(Ph_2C=$NH)_2$][I_3] **3**, [Au(Ph_2C=$NH)_2$]BF_4·CH_2Cl_2 **5**·CH_2Cl_2 and [Ag(Ph_2C=$NH)_2$]BF_4 **6**[a]

Compound	**1a**	**1b**	**2**	**3**	**5**·CH_2Cl_2	**6**
Empirical formula	$C_{13}H_{11}AuClN$	$C_{26}H_{22}Au_2Cl_2N_2$	$C_{26}H_{22}Au_2Br_2N_2$	$C_{26}H_{22}AuI_3N_2$	$C_{27}H_{24}AuBCl_2F_4N_2$	$C_{26}H_{22}AgBF_4N_2$
M	413.64	827.29	916.21	940.12	731.16	557.14
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group (no.)	$P2_1/c$ (14)	$P2_1/n$ (14)	$P2_1/n$ (14)	*Pbcn* (60)	$P2_1/c$ (14)	$C2/c$ (15)
Crystal size/mm	0.20 × 0.30 × 0.45	0.10 × 0.15 × 0.65	0.09 × 0.12 × 0.45	0.08 × 0.15 × 0.40	0.18 × 0.30 × 0.35	0.09 × 0.16 × 0.46
a/Å	9.935(1)	9.968(1)	10.046(1)	14.326(1)	13.457(1)	18.349(1)
b/Å	5.413(1)	12.725(1)	12.918(1)	10.227(1)	14.933(1)	7.717(1)
c/Å	22.980(2)	19.016(1)	19.203(3)	17.906(2)	14.979(1)	16.785(1)
β/°	93.53(1)	94.69(1)	92.53(1)		115.98(1)	103.05(1)
U/Å^3	1233.5(3)	2402.4(5)	2489.6(5)	2623.4(4)	2705.9(4)	2311.4(3)
D_c/g cm^{-3}	2.227	2.286	2.444	2.380	1.795	1.601
F(000)	768	1536	1680	1720	1416	1120
μ(Mo-Kα)/cm^{-1}	121.1	124.3	150.0	91.5	56.8	9.2
T/ °C	−62	−62	−68	−62	−68	−68
Scan	ω	ω	ω–θ	ω	ω	ω
hkl Ranges	−12 to 12, 0–6, −29 to 25	−12 to 12, 0–15, 0–23	−12 to 12, 0–16, 0–24	0–18, 0–13, 0–22	−16 to 14, −18 to 0, −18 to 18	−22 to 7, 0–9, −20 to 20
Measured reflections	3408	4384	4880	2584	4896	3048
Unique reflections	2589	4212	4692	2580	4892	2115
Used reflections	2588	4211	4690	2571	4874	2108
R_{int}	0.0296	0.0300	0.0161	0.000	0.000	0.0137
Refined parameters	146	296	289	147	334	156
H atoms (found/calc.)	—, 11	2, 20	—, 22	—, 22	—, 24	—, 22
T_{min}, T_{max}	0.5269, 0.9931	0.5721, 0.9989	0.5316, 0.9940	0.5114, 0.9997	0.5677, 0.9997	0.9039, 0.9985
$R1$ [$F_o \geqslant 4\sigma(F_o)$]	0.0346	0.0363	0.0481	0.0251	0.0284	0.0307
*wR*2 (used reflections)	0.0915	0.0899	0.1109	0.0599	0.0664	0.0862
a, *b* in weighting scheme	0.0640, 2.9925	0.0587, 8.0508	0.0516, 45.3003	0.0275, 2.4193	0.0323, 4.2403	0.0458, 626.3666
ρ_{max}, ρ_{min}[b]/e Å^{-3}	+1.36, −2.25	+2.08, −2.08	+4.07, −3.30	+0.89, −1.39	+1.32, −0.79	+0.73, −0.38

[a] Details in common: $Z = 4$; Enraf-Nonius CAD4 diffractometer; $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]^{\frac{1}{2}}$; $w = q/2\sigma^2(F_o^2) + (ap)^2 + bp$, where $p = (F_o^2 + 2F_c^2)/3$. [b] Residual electron densities located at Au or Ag atoms.

Bis(diphenylmethanimine)gold(I) tetrafluoroborate 5. To a solution of Ph_2C=NH (101 μl, 0.60 mmol) in dichloromethane (10 cm^3) was added slowly a solution of [Au($PhCN)_2$]BF_4 (0.148 g, 0.30 mmol) in dichloromethane (5 cm^3) at −78 °C. After stirring for 30 min the solution was allowed to warm to room temperature. The solvent was removed in a vacuum and the colourless residue taken up again in dichloromethane, filtered and the filtrate layered with pentane. After several days colourless crystals of compound **5**·CH_2Cl_2 (0.135 g, 61%) were obtained, m.p. 238 °C (Found: C, 44.5; H, 3.3; N, 3.8. $C_{27}H_{24}AuBCl_2F_4N_2$ requires C, 44.4; H, 3.3; N, 3.8%). δ_H[$(CD_3)_2$CD] 10.75 (1 H, br s, NH), 7.83–7.50 (10 H, m, Ph) and 5.61 (2 H, s, CH_2Cl_2); δ_C[$(CD_3)_2$CO] 186.3 (s, C=N), 138.7 and 137.0 (s, *ipso*-C), 130.8 and 129.6 (s, *o*-C), 130.2 and 129.9 (s, *m*-C), 134.5 and 133.5 (s, *p*-C). Mass spectrum: *m*/*z* 558.5, [Au(Ph_2C=$NH)_2$]$^+$, 100; and 377.5 [Au(Ph_2C=NH)]$^+$, 23%.

Bis(diphenylmethanimine)silver(I) tetrafluoroborate 6. To a solution of $AgBF_4$ (0.290 g, 1.49 mmol) in tetrahydrofuran (15 cm^3) was added Ph_2C=NH (499 μl, 2.98 mmol) at room temperature. Immediately a white solid precipitated and after 30 min the volume of the solvent was reduced to 3 cm^3, the off-white solid was filtered off, dried, and extracted with dichloromethane (30 cm^3). Upon layering this solution with pentane colourless crystals (0.712 g, 85.9% yield) were obtained (m.p. 246 °C). The crystals were only sparingly soluble in acetone, tetrahydrofuran or dichloromethane (Found: C, 55.3; H, 3.9; N, 4.9. $C_{26}H_{22}AgBF_4N_2$ requires C, 56.1; H, 4.0; N, 5.0%). δ_H(CD_2Cl_2) 9.40 (1 H, br s, NH) and 7.60–7.34 (10 H, m, Ph); δ_C(CD_2Cl_2) 184.0 (s, C=N), 139.2 and 136.9 (br s, *ipso*-C), 133.0 and 132.5 (br s, *p*-C), 130.0–128.7 (br m, *o*- and *m*-C). Mass spectrum: *m*/*z* 471.0 and 469.0, [Ag(Ph_2-C=$NH)_2$]$^+$, 56 and 60; 287.9 and 289.9, [Ag(Ph_2C=NH)]$^+$, 100 and 94.5%.

Crystallography

Suitable crystals of compounds **1a**, **1b**, **2**, **3**, **5** and **6** were sealed into glass capillaries and used for measurement of precise cell constants and intensity data collection. During data collection three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for all six compounds. Diffraction intensities were corrected for Lorentz-polarization and absorption effects (empirically). The structures were solved by direct methods and refined by full-matrix least-squares calculations against F^2.[29] The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated in idealized positions and allowed to ride on their corresponding carbon or nitrogen atom. Their isotropic thermal parameters were tied to that of the adjacent atom by a factor of 1.5. The main experimental results are summarized in Table 1.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc.*, *Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/305.

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