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Synthesis and applications of $[Au(NCPh)_2]^+$, a versatile labile gold(I) intermediate

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The $[Au(NCPh)_2]^+$ cation has been isolated and synthesized in high yields by the oxidation of gold powder in the presence of $NOBF_4$. It represents a labile form of gold(I), which has been shown to be a valuable synthon for the synthesis of a wide range of gold(I) complexes and especially of a variety of gold(I) amines which have opened new synthetic routes for the isolation of organometallic gold(I) complexes.

Nitrile compounds of the transition metals have proved to be very useful intermediates because of their substitutional lability.[1] A typical example is *trans*-$[PdCl_2(NCPh)_2]$ which is a convenient synthetic precursor for complexes such as *trans*-$[PdCl_2(tdp)_2]$ [tdp = tris(dimethylamino)phosphine, $P(NMe_3)_3$], which cannot be prepared *via* sodium tetrachloropalladate(II) in methanol[2] or anhydrous palladium(II) chloride in benzene.[3] There are a number of other related nitrile intermediates, which have been widely used as synthetic precursors to other transition-metal compounds and shown to catalyse a variety of organic transformations. These include $[Pd(NCMe)_4][BF_4]_2$[4] and $[Mo(NO)_2(NCMe)_4][BF_4]_2$[1b] which have been synthesized by oxidising palladium metal and molybdenum hexacarbonyl, respectively, with nitrosonium tetrafluoroborate in acetonitrile.[1b] The related nitrile compounds of gold(I) have, by comparison, received little attention. This can be attributed to the absence of convenient routes to them and their sensitivity to moisture. For example, the acetonitrile solvate of gold(I), $[Au(NCMe)_2]ClO_4$, has been obtained by the direct oxidation of gold metal using $NOClO_4$, but the extreme moisture sensitivity of the compound and the juxtaposition of a thermally labile MeCN molecule and ClO_4^- makes it an unattractive intermediate.[5] In 1993 Geier and co-workers[6] reported an alternative electrochemical synthesis of $[Au(NCMe)_2]^+$. This is a smooth and safe process which eliminates the problems associated with potentially explosive perchlorates and contamination from tetraalkylammonium salts. However, the electrolytic approach requires somewhat specialised equipment and long synthesis times to build up appreciable quantities of the solvated gold(I) compound. These problems could account for the reasons why $[Au(NCMe)_2]^+$ is not commonly used as an intermediate for the syntheses of gold(I) compounds.[7]

The research presented in this paper involves the development of a solvated gold(I) complex, $[Au(NCPh)_2]^+$, as a synthon for the preparation of a wide range of complexes of gold(I). Some of the complexes described have been reported previously, but were prepared in order to verify that the $[Au(NCPh)_2]^+$ cation was a viable and flexible starting material. The main objective for the development of the $[Au(NCPh)_2]^+$ cation was to establish new classes of gold(I) complexes co-ordinated to nitrogen-donor ligands, which have been neglected previously due to the lack of suitable starting materials. The possible uses of these complexes in the synthesis and characterisation of new classes of organometallic gold(I) compounds were also investigated and will be discussed briefly.

Results and Dicussion

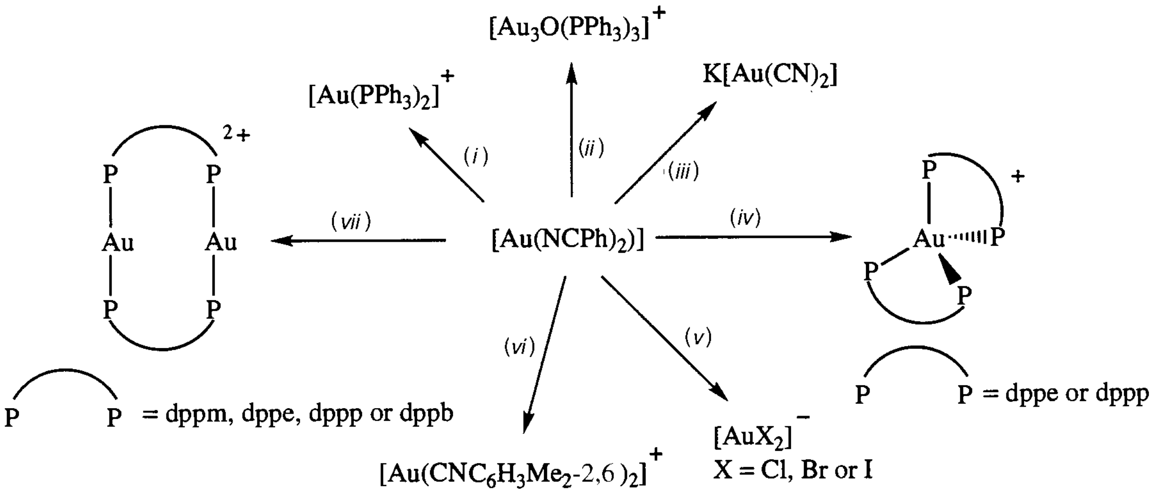
Synthesis of the $[Au(NCPh)_2]^+$ cation

The problem associated with potentially explosive perchlorates was eliminated by using $NOBF_4$ as the oxidising reagent.[8] Little is known concerning the mechanism of the reaction of the nitrosonium ion NO^+ when it acts as an oxidising agent and is itself reduced to nitric oxide. Addison *et al.*[9] showed that dinitrogen tetraoxide behaves similarly to the nitrosonium ion by oxidising copper, zinc and uranium in organic donor solvents, with the evolution of nitric oxide and the formation of the metal nitrate. The salt $NOBF_4$ was found to be capable of oxidising gold metal in acetonitrile to give $[Au(NCMe)_2]BF_4$. This complex was not fully characterised due to its reactivity, but was identified using infrared spectroscopy. The main problem associated with the reactivity of $[Au(NCMe)_2]^+$ is the weakly bound and volatile acetonitrile ligand. Consequently, it was decided to use a less volatile ligand, benzonitrile (b.p. 188 °C). Initially problems were encountered in optimising the reaction conditions to give high yields of $[Au(NCPh)_2]BF_4$, because $NOBF_4$ is only sparingly soluble in benzonitrile.

The $[Au(NCPh)_2]BF_4$ salt was isolated in yields of greater than 90% based on gold by heating a mixture of gold powder and $NOBF_4$ in anhydrous acetonitrile–benzonitrile (1:2) for 4 h at 80–90 °C. An excess of $NOBF_4$ is necessary because of its relatively low solubility and its degradation in the MeCN and PhCN solvents when heated. The compound is precipitated upon addition of anhydrous toluene, as a colourless crystalline solid (see Experimental section). It is moisture sensitive, but may nonetheless be weighed out in the open laboratory and is thermally stable (decomposition 167–169 °C). The $[Au(NCPh)_2]SbF_6$ salt was prepared in an analogous manner and was recrystallised from Et_2O. Although the SbF_6^- salt is thermally similar to the corresponding BF_4^- salt (decomposition 169–170 °C) it is more stable to moisture and hence gave more reliable elemental analyses. Recently the related $[Au(NCBu^t)_2]^+$ cation has been isolated in high yields by slightly modifying the preparation described above (see Experimental section). The cation has been found to be as reactive as the gold(I) benzonitrile intermediate but more amenable to crystallisation.

Initial investigations using NO_2BF_4 or NO_2SbF_6 as alternative oxidising agents have been encouraging. The reactions proceeded in a similar fashion evolving nitrogen dioxide and the yields of $[Au(NCPh)_2]SbF_6$ are comparable to those obtained using $NOBF_4$.

All the compounds are slightly light sensitive but may be stored for several months under nitrogen at −25 °C in the dark.



Scheme 1 Solvent MeCN. (*i*) PPh_3 (in 2:1 ratio); (*ii*) PPh_3 and KOH–MeOH; (*iii*) KCN–water; (*iv*) dppe or dppp (in 2:1 ratio); (*v*) NBu^t_4; X = Cl, Br or I; (*vi*) $CNC_6H_3Me_2$-2,6; (*vii*) dppm, dppe, dppp or dppb (in 1:1 ratio)

The photosensitivity leads to the development of a pinkish colouration in the solid, presumably resulting from gold particle formation. The compounds dissolve rapidly without decomposition in acetonitrile and benzonitrile, but decompose on dissolution in other organic solvents such as acetone and ethanol. They are readily characterised by infrared spectroscopy as Nujol mulls between KBr discs. The spectra of $[Au(NCPh)_2]BF_4$ and $[Au(NCPh)_2]SbF_6$ confirmed the presence of the tetrafluoroborate and hexafluoroantimonate(V) anions, respectively, through characteristic bands at 1047 and 657 cm^{-1}, and revealed a weak band at 2295 and 2299 cm^{-1}, respectively, which may be attributed to the ν(C≡N) stretching mode. These values are higher than that for free benzonitrile (2231 cm^{-1}). This is expected for nitrile complexes since weakly antibonding electrons are removed from the σ orbital upon co-ordination to metal centres.[10] Positive FAB mass spectral data for both the BF_4^- and SbF_6^- salts indicated the presence of the parent cation $[Au(NCPh)_2]^+$ ($m/z = 403$) and a single peak for $[Au(NCPh)]^+$ ($m/z = 300$). The sensitivity and instability of $[Au(NCPh)_2]BF_4$ prevented accurate results from elemental analysis, even when the immediate analysis of a freshly prepared sample was undertaken. Although single crystals of $[Au(NCPh)_2]BF_4$ were grown by dissolving the product in the minimum volume of benzonitrile and storing the mixture at −25 °C for approximately 1 week, the crystal structure could not be determined due to desolvation and decomposition of the product. The molecular structure of a related compound $[Au(NCMe)_2]SbF_6$ which was isolated as a by-product from the synthesis of $[Au(CO)_2][Sb_2F_{11}]$ has been determined.[11]

Reactions of the $[Au(NCPh)_2]^+$ cation

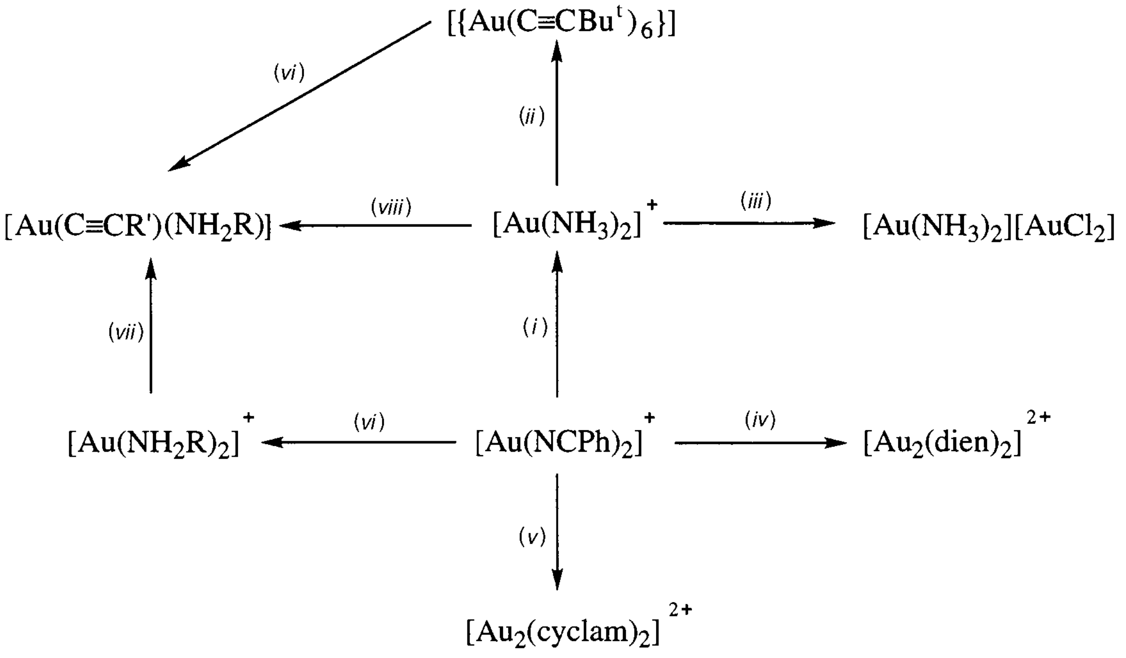
The applications of the gold(I) benzonitrile intermediate as an alternative synthon for the synthesis of gold(I) compounds are illustrated in Scheme 1. All the reactions were performed in anhydrous acetonitrile solutions. The benzonitrile ligands were readily displaced and the products were all obtained in high yields.

Synthesis of isocyanide and phosphine complexes. Gold(I) isocyanide complexes are usually formed by the reaction between $[AuCl(Me_2S)]$[12] and the required isocyanide and then precipitated with the relevant counter ion. Complexes $[Au(CNR)_2]^+$ have been widely used in the syntheses of platinum–gold cluster compounds.[13] The complex $[Au(CNC_6H_3Me_2\text{-}2,6)_2]^+$, was obtained from $[Au(NCPh)_2]^+$ in a simpler method and in virtually quantitative yields by adding 2 molar equivalents of $CNC_6H_3Me_2$-2,6 to the benzonitrile solvate in anhydrous acetonitrile. The infrared spectrum shows ν(C≡N) at 2224 cm^{-1} (lit.,[13] 2231 cm^{-1}). This compound is slightly moisture and photosensitive but can be stored for months at *ca.* −25 °C.

The ion $[O(AuPPh_3)_3]^+$,[14] which has proved to be a useful precursor for the synthesis of homo- and hetero-metallic gold cluster compounds and Schmidbaur's interstitial compounds,[15] may be formed directly from the solvated benzonitrile compound by adding 1 molar equivalent of PPh_3 in MeCN followed by dropwise addition of KOH in methanol. Although '$[Au(PPh_3)(NCMe)]^+$' was not isolated as a solid compound, $^{31}P\text{-}\{^1H\}$. NMR studies carried out in CD_3CN provide strong evidence for the formation of '$[Au(PPh_3)(NCCD_3)]BF_4$' *in situ* [δ 29.2 (s)].[14] The salt $[Au(PPh_3)_2]BF_4$[16] was prepared in an analogous manner, when 2 molar equivalents of triphenylphosphine were added to the benzonitrile complex [$^{31}P\text{-}\{^1H\}$ NMR (CD_2Cl_2) δ 45.0 (s)]. The '$[Au(PPh_3)]^+$' cation has been widely used in capping reactions in cluster chemistry and is more usually formed by the addition of silver or thallium salts to $[Au(PPh_3)Cl]$.[17] The synthesis from $[Au(NCPh)_2]^+$ could be extended to other gold(I) phosphine cations, and eliminates the use of halide extractors which can sometimes interfere with subsequent steps of the reaction.[18]

The benzonitrile ligands in $[Au(NCPh)_2]BF_4$ can be readily displaced by neutral bidentate ligands to give either the mononuclear cationic phosphine complexes $[Au(dppe)_2]^+$ and $[Au(dppp)_2]^+$,[19] or the binuclear complexes $[Au_2(dppm)_2]^{2+}$, $[Au_2(dppe)_2]^{2+}$ and $[Au_2(dppb)_2]^{2+}$ (ref. 20) when the mole ratio of phosphine to $[Au(NCPh)_2]BF_4$ was reduced to 1:1 (dppm, dppe, dppp and dppb are abbreviations for bis(diphenylphosphino)-methane, -ethane, -propane and -butane respectively).

Synthesis of anionic gold(I) complexes. One of the most widely used and documented methods for preparing $K[Au(CN)_2]$[21] is by reducing an *aqua regia* solution of $HAuCl_4{\cdot}3H_2O$ with concentrated ammonia solution, to afford a yellow-brown precipitate of 'fulminating gold' which has been known to detonate when dry.[22] The explosion is accompanied by the liberation of gold, nitrogen, ammonia and water. The 'fulminating gold' is subsequently dissolved in a solution containing slightly more than the stoichiometrically required 2 equivalents of potassium cyanide to give colourless crystals of $K[Au(CN)_2]$ on standing. In $[Au(NCPh)_2]^+$ the weakly bound benzonitrile ligands may be displaced with 2 equivalents of the cyanide anions from potassium cyanide and $K[Au(CN)_2]$ is obtained in virtually quantitative yields. The infrared spectrum of the complex shows a sharp band at 2142 cm^{-1} (lit.,[23] 2141 cm^{-1}) which can be assigned to the antisymmetric ν(C≡N) stretching mode. An initial pale yellow precipitate is observed when potassium cyanide is added to the gold(I) solution; this presumably results from



Scheme 2 Formation of organometallic complexes from the gold(I) amines, where R = H or Bu^t and R′ = Ph or Bu^t. (*i*) NH_3; (*ii*) $Bu^tC{\equiv}CH$; (*iii*) $[AuCl_2]^-$; (*iv*) dien; (*v*) cyclam; (*vi*) NHR_2; (*vii*) $R'C{\equiv}CH$

the initial formation of an insoluble polymer $[Au(CN)]_n$[7] which redissolves in an excess of CN^- ions to form $K[Au(CN)_2]$.

The conventional route to anionic halide complexes is quite tedious, and involves the initial formation of gold(III) compounds followed by their reduction.[24] As part of this study it was shown that colourless crystalline anionic gold(I) complexes $[AuX_2]^-$ (X = Cl, Br or I) can also be synthesized from $[Au(NCPh)_2]^+$ in high yields, when 2 molar equivalents of NBu^n_4X are added to the benzonitrile solvate in anhydrous acetonitrile.

Synthesis of gold(I) nitrogen-containing complexes

In contrast to the chemistry of gold(I) phosphines, that of gold(I) with nitrogen-donor ligands has been relatively neglected, presumably due to the lack of suitable starting materials. The first structurally characterised gold(I) complex co-ordinated to two nitrogen-donor ligands, sodium bis(1-methylimidazolidine-2,4-dionato)aurate(I) tetrahydrate, was reported by Sadler and co-workers[25] in 1978. The complex was found to exhibit therapeutic properties as an antiinflammatory drug similar to that of the gold(I) thiolates. However, sodium bis(1-methylimidazolidine-2,4-dionato)aurate(I) tetrahydrate, which was isolated in yields of 45–60%, is photosensitive and could only be stored in solution for a few days. The isolation and crystal structure of a gold(I) complex containing one nitrogen-donor ligand, chloro(piperidine)gold(I), was also reported at the same time and revealed an interesting tetrameric arrangement of gold atoms in the solid state.[26] Some gold–ammonia complexes have been reported for example $[AuX(NH_3)_n]$ (X = Cl, Br or I, n = 1–3; X = CN, n = 1) which can be prepared when ammonia reacts with gold(I) halides[7] or cyanide.[27] The $[Au(NH_3)_2]^+$ cation has been identified in solution and its equilibrium constants measured,[28] but, surprisingly, salts of the cation have not been isolated and structurally characterised. This is particularly remarkable given the stability of $[Ag(NH_3)_2]^+$,[29] which is quoted in elementary textbooks as the paradigm for linear co-ordination and the structure of which was first investigated in 1934.[30a]

$[Au(RNH_2)_2]^+$ salts. The utilisation of $[Au(NCPh)_2]^+$ in the synthesis of gold(I) amine complexes is summarised in Scheme 2. All the reactions were performed in anhydrous acetonitrile. Salts of $[Au(NH_3)_2]^+$ are formed very rapidly and easily when ammonia gas is bubbled through a solution of $[Au(NCPh)_2]^+$[31] in acetonitrile at room temperature. The product is also obtained when a concentrated aqueous ammonia solution is added to the benzonitrile complex. The resulting colourless solution yields a crystalline material when the solvent is partially removed under reduced pressure. The BF_4^- and SbF_6^- salts can be obtained in approximately 90% yield based on gold. In contrast $[Au(NH_3)_2]SbF_6$ could not be recrystallised from a MeCN–Et_2O mixture, but could be purified by washing with organic solvents such as chloroform or dichloromethane to remove the benzonitrile liberated during the reaction. Oxidation of $[Au(NH_3)_2]X$ in acetonitrile using bromine or chlorine gave a brown uncharacterisable material. Oxidative-addition reactions carried out using methyl iodide resulted in the recovery of $[Au(NH_3)_2]X$ even when an excess of MeI was used. The positive FAB mass spectrum of $[Au(NH_3)_2]BF_4$ shows a single parent-ion peak for $[Au(NH_3)_2]^+$ (m/z = 231), but a peak corresponding to $[Au(NH_3)]^+$ was not observed. The related amine complexes $[Au(NH_2R)_2]BF_4$ (R = Me, Et or Bu^t) have been synthesized by displacement of the weakly bound benzonitrile ligand from $[Au(NCPh)_2]^+$ with 2 molar equivalents of the appropriate amine. The complex $[Au(NH_2Bu^t)_2]BF_4$ is obtained in high yield as a colourless crystalline material when recrystallised from a EtOH–Et_2O mixture and can be stored in the dark at *ca.* −25 °C without decomposition. The positive FAB mass spectrum shows a single parent ion peak for $[Au(NH_2Bu^t)_2]^+$ (m/z = 343), but no peak is observed for the $[Au(NH_2Bu^t)]^+$ ion. Single crystals suitable for X-ray crystallographic analysis were grown from EtOH–Et_2O, but the process was slowed down by lowering the temperature to −25 °C. The crystallographic data which were collected from several independent crystals could not be solved, presumably due to the highly symmetrical nature of the product. The NH_2Me and NH_2Et derivatives are stable in acetonitrile solution, but extremely moisture sensitive when isolated as solids from MeCN–Et_2O. The relative stabilities of the compounds are $Bu^t \gg Et > Me$, presumably due to loss of the weakly co-ordinated and volatile amines, though they have been characterised by infrared and positive-ion FAB mass spectroscopy.

Small cubic shaped crystals of $[Au(NH_3)_2]Br$ were obtained by layering a solution of $[NBu_4][AuBr_2]$[31] in acetonitrile under

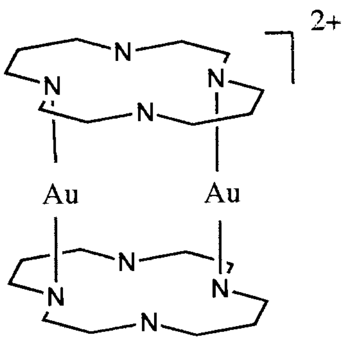


Fig. 1 Molecular structure of the dimer $[Au_2(cyclam)_2]^{2+}$

an atmosphere of NH_3 gas. The molecular structure and crystal packing of $[Au(NH_3)_2]Br$ have been described in some detail.[32]

Relatively few gold(I) compounds of pyridine (py) have been reported. The first examples, $[Au(py)_2][AuX_2]$ (X = Br or I), were reported by Strähle and co-workers[33] in 1982 and revealed interesting stacked chains in a one-dimensional lattice. The complex $[Au(py)_2]BF_4$ is obtained in high yields from $[Au(NCPh)_2]^+$ as a colourless crystalline material and recrystallised from a MeCN–Et_2O mixture. The FAB mass spectrum shows single parent-ion peaks for $[Au(py)_2]^+$ and $[Au(py)]^+$ at $m/z = 355$ and 276, respectively. Single crystals suitable for X-ray crystallographic analysis were grown by slow diffusion of Et_2O into an acetonitrile solution containing the compound or by simply dissolving in the minimum volume of EtOH and leaving at *ca.* −25 °C for 1 week. The complex crystallises in the tetragonal crystal system, where $a = 13.2607$ and $c = 140.594$ Å, but the structure could not be solved. The ion $[Au(pip)_2]^+$ (pip = piperidine) was also prepared conveniently in a one-step synthesis using $[Au(NCPh)_2]^+$. The BF_4^- salt is isolated in high yield as colourless needles when crystallised at −25 °C from a CH_2Cl_2–Et_2O mixture.

$[Au_2(dien)_2][BF_4]_2$ and $[Au_2(cyclam)_2][BF_4]_2$. Elder and co-workers[34] have examined and studied the structures of a number of gold-containing arthritis drugs and related gold-containing compounds, using both extended X-ray absorption spectroscopy (EXAFS) and single-crystal X-ray diffraction techniques. One of the complexes reported was $[Au^{III}(dien)Cl_3]$[34c] (dien = diethylenetriamine), which is somewhat surprising given that Au^{III} has been well documented to be toxic to living tissue. As part of an ongoing study it was decided to employ dien in the synthesis of a gold(I) analogue. Similarly, the study of the binding of cyclam (1,4,8,11-tetraazacyclotetradecane) to Au^I was undertaken because there have been relatively few examples of Au^I encapsulated by a cavity of donor ligands such as nitrogen. Schröder and co-workers[35] reported one of the few examples where Au^I is encapsulated by a cavity generated by [18]aneS_6 (1,4,7,10,13,16-hexathiacyclooctadecane),[35b] and demonstrated that the co-ordination geometry depends on the size of the macrocyclic ring.[35c] The gold(I) benzonitrile intermediate has been employed effectively in the synthesis of $[Au_2(cyclam)_2]^{2+}$[36] and $[Au_2(dien)_2]^{2+}$.[37] Both complexes have been characterised by IR, NMR and FAB mass spectroscopy. The FAB mass spectrum of $[Au_2(dien)_2][BF_4]_2$ shows a parent-ion peak which can be attributed to $[Au_2(dien)_2]^{2+}$ ($m/z = 300$, 45%), and a peak corresponding to $[Au(dien)_2]^+$ ($m/z = 403$, 10%). Reactions carried out with other similar ligands such as $H_2N(CH_2)_3NH(CH_2)_3NH_2$ and $N(CH_2CH_2NH_2)_3$ resulted in the formation of oils which could not be characterised. The expected isotope distribution for the parent cation $[Au_2(cyclam)_2]^{2+}$ ($m/z = 397$, 45%) was observed. An interesting array of $[Au(cyclam)]^+$ aggregates of up to five gold atoms with different cyclam ratios was also observed in the FAB mass spectrum, which may suggest the existence of low-nuclearity homonuclear clusters stabilised by the cyclam ligands. This observation has prompted attempts to utilise the remaining pair of nitrogen atoms of the cyclam, by treating them with another equivalent of $[Au(NCPh)_2]^+$. However, many attempts to isolate and characterise the higher-nuclearity product(s) have been unsuccessful. Similarly oxidative addition reactions using bromine gave an uncharacterisable amorphous brown material. Reactions with similar nitrogen-donor ligands, such as cyclen (1,4,7,10-tetraazacyclododecane) and 1,4,7-triazacyclononane, have resulted in $[Au(NCPh)_2]^+$ undergoing reduction to yield gold mirrors.

The single-crystal structures of the dien and cyclam complexes (Figs. 1 and 2) have been reported elsewhere and will not be discussed in detail here.[36,37]

All the gold(I)–nitrogen compounds mentioned above are soluble in polar organic solvents such as acetone or acetonitrile, but only sparingly soluble in ethanol. They are slightly photosensitive, but may be stored for prolonged periods under nitrogen in the dark at *ca.* −25 °C, without deterioration. All these gold(I) complexes have been fully characterised by elemental analyses, FAB mass and infrared spectroscopy.

Uses of the $[Au(NH_2R)_2]^+$ salts

The thermally labile and basic nitrogen-donor ligands of $[Au(NH_2R)_2]^+$ have also been exploited in the synthesis of a range of alkynylgold(I) complexes, $[Au(C\equiv CR')(NH_2R)]$ (R = H or Bu^t, R′ = Ph or Bu^t). These are colourless and their detailed spectroscopic properties and physical properties are described in the Experimental section. When the reaction was repeated with $[Au(NH_3)_2]^+$ and $Bu^tC\equiv CH$, yellow material precipitated and the absence of nitrogen in the elemental analysis suggested that ammonia was no longer co-ordinated to the gold(I) centre and that the product was best formulated as $[\{Au(C\equiv CBu^t)\}_n]$. In the early 1960s Coates and Parkin[38] reported a similar compound, which was prepared by reducing gold(III) with sulfur dioxide in the presence of $Bu^tC\equiv CH$. The above route surprisingly led to the isolation and crystal structure of the first gold(I) self-assembled [2]catenane complex $[\{Au(C\equiv CBu^t)\}_6]$.[39]

In contrast to the vast number of stacked and mixed-valence palladium and platinum complexes, there are relatively few examples of the corresponding gold complexes. Complexes such as $Cs_2[Au^ICl_2][Au^{III}Cl_4]$[40] and $[Au^{III}(Hdmg)_2]^+[Au^ICl_2]^-$[41] (Hdmg = dimethylglyoximate) were initially considered to be gold(II) species, but the X-ray crystallographic analysis revealed the molecular structures to consist of independent ions, square-planar Au^{III} and linear Au^I, with each unit stacked to form a chain of gold atoms. The majority of mixed-valence gold complexes mentioned form black crystals. Unlike the mixed-valence platinum-group metal complexes, the gold complexes are electrical insulators at room temperature and atmospheric pressure, due to the firmly localised valencies. Other related stacked gold(I) complexes include $[Au(pdma)_2]^+[Au(C_6F_5)_2]^-$[42] [pdma = $C_6H_4(AsMe_2)_2$-1,2] and $[Au(S_2CNR_2)_2]^+[AuBr_2]^-$,[43] consisting of independent cations and anions. As an ongoing study in the uses of linear gold(I) amine complexes, the related gold(I) complex $[Au(NH_3)_2]^+[AuCl_2]^-$ was synthesized and isolated. The metallic looking material was isolated in good yield by slow addition of the constituent cations and anions in an acetonitrile solution. The complex is insoluble in both polar and non-polar solvents and can be stored under nitrogen without deterioration. It has been characterised by infrared spectroscopy which revealed bands consisting of the superposition of the spectra of the two constituent ions.

Conclusion

Replacing the volatile ligand in the $[Au(NCMe)_2]^+$ cation with the less volatile benzonitrile has led to samples of [Au-

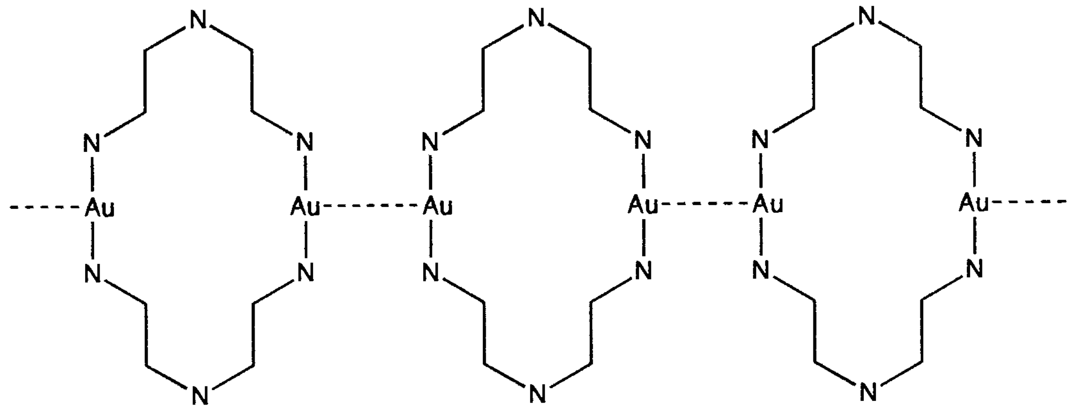


Fig. 2 A pair of weakly linked macrocyclic dimers in the structure of [{Au$_2$(dien)$_2$(BF$_4$)$_2$·EtOH}$_n$]

(NCPh)$_2$]BF$_4$ with improved moisture and thermal stabilities. It may be used as a reactive source of gold(I) in the syntheses of chelated, bridged and anionic complexes and the relevant reactions are summarised in Scheme 1.

The [Au(NCPh)$_2$]$^+$ cation has also been employed successfully in the syntheses of a series of gold(I) amine complexes and especially in the formation and isolation of [Au(NH$_3$)$_2$]$^+$ the structure of which has eluded chemists over the last century. In many cases the gold(I) amines are extremely crystalline, and although the majority of the crystallographic data were collected at low temperature (*ca.* 150 K) many attempts at solving the molecular structures were hindered due to the highly symmetrical ligands which result in crystallographic disorder. Attempts to lower the symmetry by using substituted ligands for example 3-bromopyridine have also given extremely crystalline materials, but unfortunately the crystals were not suitable for single-crystal analysis. The longer gold–gold contacts exhibited in [Au(NH$_3$)$_2$]Br when compared with the silver–silver contacts in [Ag(NH$_3$)]BF$_4$ and other simple gold(I) compounds {for example [Au(C≡CPh)(NH$_2$Pr^i)] shows short Au···Au contacts equal to 3.27 Å}[44] are particularly surprising in view of the 'aurophilicity' effect which has been discussed extensively by Schmidbaur.[45] The pronounced tendency of gold(I) linear fragments to approach each other in such a manner that the gold–gold contacts begin to approximate to those distances found in the bulk metal (2.88 Å) is widespread and has been attributed to relativistic effects and d–s hybridisation phenomena.[46] Therefore, it is rather surprising that the Au···Au contacts in the present structure are longer than the corresponding ones for the related silver compounds.[30]

The [Au(NCPh)$_2$]$^+$ [31] cation which has been discussed above in the syntheses of a variety of gold(I) amines[32] has overcome many of the traditional difficulties and has opened new synthetic doorways for the synthesis of organometallic gold(I) complexes. It has been demonstrated that the gold(I) amines, [Au(NH$_2$R)$_2$]$^+$ (R = H or Bu^t) can be exploited successfully in the syntheses of a range of gold(I) organometallic complexes, [Au(C≡CR)(NH$_3$)] (R = Ph or Bu^t), in a convenient one-step reaction by simply replacing the thermally labile and basic amine groups with RC≡C$^-$ anions (R = Ph or Bu^t), as summarised in Scheme 2.

Experimental

All chemicals were obtained from Aldrich, ammonia gas from BOC Limited and used as received. Organic solvents were of reagent grade, dried by published procedures,[47] distilled under N$_2$ and vacuum-degassed before use, except for benzonitrile which was obtained from Aldrich as an anhydrous solvent. All reactions were routinely carried out under N$_2$ using standard Schlenk-line techniques.

Infrared spectra in the 4000–220 cm^{-1} region were recorded on a Perkin-Elmer 1720 Fourier-transform spectrometer as KBr pellets or as Nujol mulls between KBr plates, NMR spectra on a JEOL JNM-EX270 FT-NMR spectrometer at 25 °C; ^{1}H and ^{31}P-{^{1}H} chemical shifts were referenced to tetramethylsilane and 85% phosphoric acid (H$_3$PO$_4$) in water, respectively. Fast atom bombardment (FAB) mass spectra were recorded on a VG AutoSpec-Q instrument using 3-nitrobenzyl alcohol as matrix.

Syntheses

[Au(NCPh)$_2$]X (X = BF$_4$ or SbF$_6$). *By* NOBF$_4$ *oxidation.* Gold powder (1.503 g, 7.63 mol) was added to a Schlenk vessel containing NOBF$_4$ (0.407 g, 4.0 mol), followed by anhydrous benzonitrile (30 cm^3) under N$_2$ to give a colourless suspension. The minimum volume of acetonitrile (*ca.* 15 cm^3) was added to dissolve the NOBF$_4$, giving a pale yellow solution. The resulting mixture was heated between 80 and 90 °C; after *ca.* 30 min a pale yellow vapour was observed, presumably resulting from the formation of nitric oxide and its subsequent reaction with traces of oxygen to form nitrogen dioxide. After heating for 4 h the acetonitrile was removed under reduced pressure and the solution filtered using a Teflon cannula. The pale yellow solution was layered with toluene (10 cm^3) and agitated to give a homogeneous solution. The process was repeated until a permanent colourless microcrystalline material was observed. A large excess of toluene (*ca.* 50 cm^3) was then added to ensure all the [Au(NCPh)$_2$]BF$_4$ had precipitated. The solution was then rapidly filtered using a Teflon cannula under N$_2$ and the product dried under reduced pressure. Yield: 1.508 g (90% based on gold). $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 2295s [ν(C≡N)], and 1047s (br) [ν(BF)]. Positive-ion FAB mass spectrum: *m/z* = 403 {100%, [Au(NCPh)$_2$]$^+$}.

By NO$_2$BF$_4$ *oxidation.* The procedure was very similar to that described above, except that NO$_2$BF$_4$ was used. Yield of [Au(NCPh)$_2$]BF$_4$ 87%. The IR spectrum of the product was identical to that given above.

By NO$_2$SbF$_6$ *oxidation.* Gold powder (1.48 g, 7.51 mol) was added to a Schlenk vessel containing NO$_2$SbF$_6$ (0.49 g, 1.73 mol), followed by anhydrous benzonitrile (30 cm^3) under N$_2$ to give a pale yellow solution. The mixture was heated between 75 and 80 °C; after *ca.* 30 min a pale yellow vapour was observed presumably resulting from the formation of nitrogen dioxide. After heating for 3 h the solution was filtered using a Teflon cannula. A large excess of Et$_2$O (*ca.* 50 cm^3) was added to the pale yellow solution to precipitate colourless microcrystals of [Au(NCPh)$_2$]SbF$_6$. The solution was then filtered quickly using a Teflon cannula under N$_2$ and the product dried under reduced pressure. Yield: 0.74 g (72% based on gold) (Found: C, 25.3; H, 1.5; N, 4.2. C$_{14}$H$_{10}$AuF$_6$N$_2$Sb requires C, 26.3; H, 1.6; N, 4.4%). $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 2299s [ν(C≡N)] and 657s [ν(SbF)]. *m/z* = 403 {100%, [Au(NCPh)$_2$]$^+$}.

$[Au(NCBu^t)_2]BF_4$. Gold powder (1.51 g, 7.68 mol) was added to a Schlenk containing $NOBF_4$ (0.31 g, 2.66 mol), followed by anhydrous acetonitrile (30 cm^3). The resulting mixture was heated between 80 and 90 °C for 4 h, to give a pale yellow suspension which was concentrated to *ca.* 10 cm^3 under reduced pressure and filtered using a Teflon cannula. The compound $NCBu^t$ (0.44 g, 5.32 mol) was subsequently added and stirred for 10 min. A large volume of Et_2O (*ca.* 50 cm^3) was added to precipitate colourless microcrystals of $[Au(NCBu^t)_2]BF_4$, which were filtered off and dried under reduced pressure. Yield: 0.87 g (81% based on gold). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2258w [ν(C≡N)] and 1069s (br) [ν(BF)].

$[AuL_2]BF_4$ (L = PPh_3 or $CNC_6H_3Me_2$-2,6). L = PPh_3. Two equivalents of PPh_3 (0.11 g, 0.408 mmol) were added with stirring to a solution of $[Au(NCPh)_2]BF_4$ (0.10 g, 0.204 mmol) in MeCN (10 cm^3) at room temperature, to give a colourless solution. After allowing to stir for *ca.* 30 min the minimum volume of Et_2O (30 cm^3) was added, yielding colourless microcrystals, which were filtered off, washed with cold EtOH (10 cm^3) and dried under reduced pressure. Yield: 0.15 g (93%) (Found: C, 54.0; H, 3.4. $C_{36}H_{30}AuBF_4P_2$ requires C, 53.5; H, 3.7%). $^{31}P-\{^1H\}$ NMR (CD_2Cl_2): δ 45.0 (s).

L = $CNC_6H_3Me_2$-2,6. The same procedure as above was employed using $CNC_6H_3Me_2$-2,6 (0.054 g, 0.408 mmol) except after allowing to stir for *ca.* 30 min Et_2O (40 cm^3) was added and left at −25 °C for 24 h, to give colourless crystals. The solution was filtered under N_2 and the crystals dried under reduced pressure. The complex $[Au(CNC_6H_3Me_2\text{-}2,6)_2]BF_4$ can also be crystallised by removing acetonitrile slowly from an acetonitrile–toluene mixture. Yield: 0.094 g (84% based on gold) (Found: C, 39.5; H, 3.1; N, 5.8. $C_{18}H_{18}AuBF_4N_2$ requires C, 39.6; H, 3.3; N, 5.1%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 2224vs [ν(C≡N)] (lit.,[13] 2231) and 1054vs (br) [ν(BF)]. ^1H NMR ($CDCl_3$): δ 2.5 (s, 6 H, 2Me), 7.2 (d, 2 H, Ph) and 7.4 (t, 1 H, Ph).

$[O(AuPPh_3)_3]BF_4$. Triphenylphosphine (0.161 g, 0.61 mmol) was added with continuous stirring to a solution of $[Au(NCPh)_2]BF_4$ (0.30 g, 0.61 mmol) in MeCN (20 cm^3) at 21 °C, to give a colourless solution. After allowing to stir for *ca.* 30 min the solution was diluted with propan-1-ol (30 cm^3) and the MeCN removed under reduced pressure. Potassium hydroxide (0.0114 g, 0.203 mmol) dissolved in MeOH (5 cm^3) was added dropwise to the colourless solution containing '$[Au(PPh_3)(NCMe)]BF_4$' to give a colourless precipitate. After stirring for 30 min, the mixture was reduced to dryness and the product extracted with CH_2Cl_2 (3 × 5 cm^3). The extract was then diluted with propan-1-ol (20 cm^3) and recrystallised by removing CH_2Cl_2 slowly under reduced pressure. Yield: 0.202 g (67%) (Found: C, 44.2; H, 2.7. $C_{54}H_{45}AuBF_4OP_3$ requires C, 43.8; H, 3.0%). $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ 24.7 (s).

$[Au_2L_2][BF_4]_2$ (L = dppm, dppe, dppp or dppb). L = *dppm*. One molar equivalent of dppm (0.078 g, 0.204 mmol) was added as a solid with continuous stirring to a solution of $[Au(NCPh)_2]BF_4$ (0.10 g, 0.204 mmol) in acetonitrile (10 cm^3) at room temperature, to give a colourless solution. After allowing to stir for *ca.* 30 min the solution was reduced to dryness under reduced pressure, and subsequently the product was washed with EtOH (10 cm^3) and recrystallised from MeCN–Et_2O. Yield: 0.174 g (64%) (Found: C, 44.5; H, 3.2. $C_{50}H_{44}Au_2B_2F_8P_4$ requires C, 45.0; H, 3.3%). $^{31}P-\{^1H\}$ NMR (CD_3CN): δ 36.2 (s) [lit.,[20a] 35.1 (s) for the ClO_4^- salt].

L = *dppe*. The method described above was employed for dppe (0.081 g, 0.204 mmol), and the product was recrystallised from CH_2Cl_2–Et_2O or CH_2Cl_2–hexane. Yield: 0.20 g (72%) (Found: C, 44.9; H, 3.4. $C_{52}H_{48}Au_2B_2F_8P_4$ requires C, 45.8; H, 3.5%). $^{31}P-\{^1H\}$ NMR (CD_3CN): δ 38.4 (s).

L = *dppp*. The method described above was employed for dppp (0.084 g, 0.204 mmol), and the product was recrystallised from CH_2Cl_2–Et_2O or CH_2Cl_2–hexane. Yield: 0.187 g (66%) (Found: C, 46.3; H, 3.4. $C_{54}H_{52}Au_2B_2F_8P_4$ requires C, 46.6; H, 3.7%). $^{31}P-\{^1H\}$ NMR (CD_3CN): δ 41.5 (s).

L = *dppb*. A colourless precipitate was obtained when dppb (0.078 g, 0.204 mmol) was added with stirring to a solution of $[Au(NCPh)_2]BF_4$ (0.10 g, 0.204 mmol) in acetonitrile (10 cm^3) at room temperature. The precipitate was subsequently filtered off, dried under reduced pressure and washed with EtOH (3 × 5 cm^3). Yield: 0.235 g (81%) (Found: C, 47.8; H, 4.0. $C_{56}H_{56}Au_2B_2F_8P_4$ requires C, 47.4; H, 3.9%). $^{31}P-\{^1H\}$ NMR (CD_3CN): δ 41.9 (s).

$[Au_2(dppe)_2][ClO_4]_2$. One equivalent of dppe (0.035 g, 0.204 mmol) was added to a colourless solution of $[Au(NCPh)_2]BF_4$ (0.10 g, 0.204 mmol) in acetonitrile (10 cm^3) at room temperature. After stirring for 30 min the colourless solution was reduced to dryness, redissolved in methanol (20 cm^3) and filtered *via* a Teflon cannula. Lithium perchlorate (0.022 g, 0.204 mmol) dissolved in methanol (5 cm^3) was added to give a pale yellow solution. This was concentrated to *ca.* 5 cm^3 to give a colourless precipitate. The product was filtered off, washed several times with Et_2O (3 × 10 cm^3) and purified by recrystallisation from a MeCN–Et_2O mixture. Yield: 0.10 g (72%) (Found: C, 44.7; H, 3.3. $C_{52}H_{48}Au_2Cl_2O_8P_2$ requires C, 45.0; H, 3.5%). $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ 39.0 (s) [lit.,[20b] 44.6 (s) at −90 °C]. It is not clear why there is a discrepancy in observed and literature chemical shifts for this specific compound. For the other compounds previously reported the chemical shifts agree to within 1.0 ppm although different anions are present. This ClO_4^- salt has a $^{31}P-\{^1H\}$ chemical shift only 0.6 ppm different from the corresponding BF_4^- salt described above.

$[AuL_2]BF_4$ (L = dppe or dppp). L = *dppe*. Two equivalents of dppe (0.16 g, 0.408 mmol) were added to a colourless solution of $[Au(NCPh)_2]BF_4$ (0.10 g, 0.204 mmol) in acetonitrile (10 cm^3) at room temperature. After stirring for 30 min the colourless solution was filtered, reduced to dryness and the product recrystallised from a EtOH–hexane or CH_2Cl_2–hexane mixture. Yield: 0.159 g (76%) (Found: C, 57.5; H, 4.5. $C_{52}H_{48}AuBF_4P_4$ requires C, 57.8; H, 4.4%). $^{31}P-\{^1H\}$ NMR (CD_3CN): δ 21.4 (s) [lit.,[19b] 20.8 (s) for Cl^- salt].

L = *dppp*. A colourless solution was obtained when dppp (0.17 g, 0.408 mmol) was added with stirring to a solution of $[Au(NCPh)_2]BF_4$ (0.10 g, 0.204 mmol) in acetonitrile (10 cm^3) at room temperature. The solution was filtered, reduced to dryness and the residue subsequently washed with EtOH (3 × 5 cm^3). Yield: 0.121 g (54%) (Found: C, 58.4; H, 4.6. $C_{54}H_{52}Au_2B_2F_8P_2$ requires C, 58.5; H, 4.7%). $^{31}P-\{^1H\}$ NMR (CD_3CN): δ −1.7 (s) [lit.,[19b] −2.7 (s) for Cl^- salt].

$[NBu^n_4][AuX_2]$ (X = Cl, Br or I). X = Cl *or* Br. Two equivalents of NBu^n_4X (0.408 mmol) were added with stirring to a solution of $[Au(NCPh)_2]BF_4$ (0.10 g, 0.204 mmol) in MeCN (10 cm^3) at room temperature, to give a colourless solution. After allowing to stir for *ca.* 30 min the solution was reduced to dryness under vacuum to give an oil. This was redissolved in the minimum volume of EtOH (5 cm^3) and diluted with a five-fold excess of Et_2O (25 cm^3). The resultant mixture was left at *ca.* −25 °C for 24 h, to give colourless needles. $\tilde{\nu}_{max}/cm^{-1}$ (polyethene) 351w [ν(Au–Cl)] (lit., 350) and 255m [ν(Au–Br)] (lit.,[24a] 254).

X = I. The same method as that described above was used (using 0.150 g, 0.408 mmol of NBu^n_4I). A pale yellow solution was observed, and the product crystallised by diluting the acetonitrile solution with a ten-fold excess of Et_2O, to afford pale yellow crystals. Yield: 0.141 g (85%) (Found: C, 27.8; H, 5.1; N, 2.0. $C_{16}H_{36}AuI_2N$ requires C, 27.7; H, 5.2; N, 2.0%). Lit.,[24a] 210 cm^{-1}.

[N(PPh$_3$)$_2$][AuCl$_2$]. This complex can be obtained in high yields by the same method used to prepare [NBu$^n_4$][AuI$_2$] but using [N(PPh$_3$)$_2$]Cl (0.23 g, 0.408 mmol) and recrystallising from a MeCN–Et$_2$O or a CH$_2$Cl$_2$–Et$_2$O mixture. Yield: 0.139 g (85%) (Found: C, 53.4; H, 3.8; N, 1.7. C$_{36}$H$_{30}$AuCl$_2$NP$_2$ requires C, 53.6; H, 3.7; N, 1.7%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 350w [ν(Au–Cl)] (lit.,[24c] 350).

K[Au(CN)$_2$]. Potassium cyanide (0.030 g, 0.461 mmol) dissolved in water (*ca.* 10 cm^3) was added dropwise to a solution of [Au(NCPh)$_2$]BF$_4$ (0.10 g, 0.204 mmol) in MeCN (5 cm^3) at room temperature, immediately forming a pale yellow precipitate. After stirring for 1 min the precipitate dissolved to give a colourless solution. The volume was concentrated by gentle heating under atmospheric pressure to give colourless microcrystals of K[Au(CN)$_2$], which were filtered off and air dried. Yield: 0.043 g (73%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 2142vs [ν(C≡N)] (lit.,[23] 2141).

[Au(NH$_3$)$_2$]BF$_4$. A steady stream of NH$_3$ gas was bubbled through a solution of [Au(NCPh)$_2$]BF$_4$ (0.1 g, 0.204 mmol) in MeCN (*ca.* 20 cm^3) for 30 min at ambient temperature. The resultant colourless solution was concentrated to *ca.* 5 cm^3, filtered *via* a Teflon cannula and precipitated with Et$_2$O (30 cm^3) to give a colourless amorphous solid. After filtering the product was washed several times with Et$_2$O (3 × 10 cm^3) and dried under reduced pressure. The complex [Au(NH$_3$)$_2$]BF$_4$ can also be recrystallised from a MeCN–Et$_2$O mixture. Yield: 0.059 g (91% based on gold) (Found: H, 1.4; N, 8.6. H$_6$AuBF$_4$N$_2$ requires H, 1.9; N, 8.8%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3303s, 3240s, 3178s [ν(N–H)], 1320vs, 1283vs [δ(N–H)], 1055vs (br) [ν(B–F)] and 523s [ν(Au–N)]. *m/z* = 231 {100%, [Au(NH$_3$)$_2$]$^+$}.

[Au(NH$_3$)$_2$]SbF$_6$. Ammonia gas was bubbled through a solution of [Au(NCPh)$_2$]SbF$_6$ (0.1 g, 0.156 mmol) in MeCN (*ca.* 20 cm^3) for 30 min at ambient temperature. The resultant colourless solution was filtered using a Teflon cannula and reduced to dryness to give colourless crystals, which were then washed with CH$_2$Cl$_2$ (3 × 5 cm^3), filtered and dried under reduced pressure. Yield: 0.063 g (87% based on gold) (Found: H, 1.0; N, 6.0. H$_6$AuF$_6$N$_2$Sb requires H, 1.3; N, 6.0%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3298s, 3138 (br) [ν(N–H)], 1273s, 1257w [δ(N–H)] and 665 (br) [ν(SB–F)]. *m/z* = 231 {100%, [Au(NH$_3$)$_2$]$^+$}.

[Au(NH$_2$Bu^t)$_2$]BF$_4$. Two molar equivalents of NH$_2$Bu^t (0.042 cm^3, 0.408 mmol) were added dropwise to a stirred solution of [Au(NCPh)$_2$]BF$_4$ (0.1 g, 0.204 mmol) in MeCN (*ca.* 20 cm^3) at room temperature. After stirring for 30 min the resultant colourless solution was reduced to dryness to give colourless crystals. These were redissolved in the minimum volume of EtOH, filtered *via* a Teflon cannula and precipitated using an excess volume of Et$_2$O. Single crystals of [Au(NH$_2$Bu^t)$_2$]BF$_4$ can be obtained by diluting an ethanol solution of [Au(NH$_2$Bu^t)$_2$]BF$_4$ with a large excess of Et$_2$O (five fold) and cooling to *ca.* −25 °C. Yield: 0.057 g (65%) (Found: C, 22.4; H, 5.0; N, 6.5. C$_{10}$H$_{10}$AuBF$_4$N$_2$ requires C, 22.4; H, 5.1; N, 6.5%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3289vs, 3252vs, 3228vs [ν(N–H)], 2965vs, 2934s, 2902s [ν(C–H)], 1371vs, 1211s [δ(N–H)], 1055vs (br) [ν(B–F)], 533w and 522w [ν(Au–N)]. *m/z* = 343 {100%, [Au(NH$_2$Bu^t)$_2$]$^+$}.

[Au(NH$_2$R)$_2$]BF$_4$ (R = Me or Et). These derivatives can be prepared and recrystallised in an analogous manner to that for [Au(NH$_2$Bu^t)$_2$]BF$_4$. Although the complexes are extremely moisture sensitive and could not be characterised by elemental analyses, they have been fully characterised by infrared and FAB mass spectroscopy.

[Au(NH$_2$Me)$_2$]BF$_4$: $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3321s, 3220vs, 3189vs, 3106vs [ν(N–H)], 2943s, 2894vs [ν(C–H)], 1298m, 1262m [δ(N–H)], 1084vs (br) [ν(B–F)], 533m and 521m [ν(Au–N)]; *m/z* = 259 {100%, [Au(NH$_2$Me)$_2$]$^+$}.

[Au(NH$_2$Et)$_2$]BF$_4$: $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3306s, 3258s, 3216s, 3175s [ν(N–H)], 2971s [ν(C–H)], 1241s [δ(N–H)], 1084vs (br) [ν(B–F)], 534s, 522s [ν(Au–N)]; *m/z* = 287 {100, [Au(NH$_2$Et)$_2$]$^+$} and 242 {10%, [Au(NH$_2$Et)]$^+$}.

[Au(py)$_2$]BF$_4$. Pyridine (0.04 cm^3, 0.506 mmol) was added with continuous stirring to a solution of [Au(NCPh)$_2$]BF$_4$ (0.1 g, 0.204 mmol) in acetonitrile (10 cm^3) at room temperature, to give a colourless solution. After stirring for 30 min the solution was filtered under N$_2$ *via* a Teflon cannula and the volume concentrated to *ca.* 5 cm^3. Diethyl ether (*ca.* 20 cm^3) was added to precipitate colourless microcrystalline [Au(py)$_2$]BF$_4$. The complex can also be recrystallised from EtOH. Yield: 0.80 g (89%) (Found: C, 27.3; H, 2.1; N, 6.3. C$_{10}$H$_{10}$AuBF$_4$N$_2$ requires C, 27.2; H, 2.3; N, 6.3%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3306s, 3258s, 3216s, 3175s [ν(N–H)], 2971s [ν(C–H)], 1241s [δ(N–H)], 1084vs (br) [ν(B–F)], 534s and 522s [ν(Au–N)]. *m/z* = 355 {95, [Au(py)$_2$]$^+$} and 276 {10%, [Au(py)]$^+$}.

[Au(pip)$_2$]BF$_4$. To a colourless solution of [Au(NCPh)$_2$]BF$_4$ (0.1 g, 0.204 mmol) in MeCN (10 cm^3) at room temperature, was added dropwise piperidine (0.04 cm^3, 0.408 mmol) with continuous stirring. After 30 min the volume was reduced to dryness under reduced pressure, to give a colourless oil. This was subsequently redissolved in the minimum volume of CH$_2$Cl$_2$ (10 cm^3) and diluted with a large excess of Et$_2$O (*ca.* 50 cm^3), to give crystalline [Au(pip)$_2$]BF$_4$ when stored at −25 °C for *ca.* 10 d. This salt can also be recrystallised from a PhCN–Et$_2$O mixture. Yield: 0.078 g (85%) (Found: C, 26.5; H, 4.6; N, 6.1. C$_{10}$H$_{20}$AuBF$_4$N$_2$ requires C, 26.5; H, 4.8; N, 6.2%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3192s, 3104w, 3070w [ν(N–H)], 2937s, 2863s [ν(C–H)], 1059vs (br) [ν(B–F)], 533m and 521m [ν(Au–N)]. *m/z* = 387 {100%, [Au(py)$_2$]$^+$}.

[Au$_2$(dien)$_2$][BF$_4$]$_2$. Diethylenetriamine (0.022 cm^3, 0.204 mmol) was added dropwise to a solution of [Au(NCPh)$_2$]BF$_4$ (0.10 g, 0.204 mmol) in acetonitrile (10 cm^3) at room temperature. After stirring for 45 min the colourless solution was reduced to dryness under reduced pressure to give a colourless oil, which was subsequently washed with CH$_2$Cl$_2$ (3 × 5 cm^3) to remove displaced benzonitrile and any excess of dien. The precipitate was redissolved in the minimum volume of acetonitrile (*ca.* 10 cm^3), filtered *via* a Teflon cannula and crystallised by the addition of Et$_2$O (40 cm^3) affording colourless microcrystalline [Au$_2$(dien)$_2$][BF$_4$]$_2$. Yield: 0.127 g (81% based on gold) (Found: C, 13.0; H, 2.6; N, 10.8. C$_4$H$_{11}$AuBF$_4$N$_3$ requires C, 12.5; H, 3.4; N, 10.9%).

[Au$_2$(cyclam)$_2$][BF$_4$]$_2$. The compound cyclam (0.04 g, 0.204 mmol) dissolved in the minimum volume of CH$_2$Cl$_2$ (*ca.* 5 cm^3) was added dropwise *via* a Teflon cannula to a solution of [Au(NCPh)$_2$]BF$_4$ (0.10 g, 0.204 mmol) in acetonitrile (20 cm^3) at −40 °C. After stirring for 1 h the colourless solution was allowed to warm to room temperature and concentrated to *ca.* 5 cm^3 to give a pink solution, presumably due to the formation of gold particles. The solution was filtered and [Au$_2$(cyclam)$_2$][BF$_4$]$_2$ was precipitated as an off-white amorphous material by the addition of Et$_2$O (40 cm^3). It can also be recrystallised from MeCN–Et$_2$O. Yield: 0.094 g (65%) (Found: C, 25.0; H, 4.8; N, 11.3. C$_{10}$H$_{24}$AuBF$_4$N$_4$ requires C, 24.8; H, 5.0; N, 11.6%).

[Au(NH$_3$)$_2$][AuCl$_2$]. The salt [Au(NH$_3$)$_2$]BF$_4$ (0.012 g, 0.0378 mmol) dissolved in acetonitrile (10 cm^3) was added dropwise to a solution of [NBu$_4$][AuCl$_2$] (0.0193 g, 0.0378 mmol) in acetonitrile (10 cm^3). To give a colourless crystalline material. After allowing to stir for *ca.* 30 min, the colourless precipitate was filtered off under N$_2$ *via* a Teflon cannula, subsequently washed with CH$_2$Cl$_2$ (3 × 5 cm^3) and then dried under reduced pressure. Yield: 0.0095 g (53% based on gold) (Found: H, 0.8; N, 5.6. H$_6$Au$_2$Cl$_2$N$_2$ requires H, 1.2; N, 5.6%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3307s [ν(N–H)], 1282s [δ(N–H)] and 328w [ν(Au–Cl)].

$[Au(C\equiv CPh)(NH_3]$. Phenylethyne (0.0025 cm^3, 0.228 mmol) was added dropwise to $[Au(NH_3)_2]BF_4$ (0.065 g, 0.204 mmol) dissolved in acetonitrile (10 cm^3). The colourless solution was allowed to stir for 1 h. After *ca.* 10 min a white microcrystalline solid separated, which was eventually filtered off, washed with acetonitrile (3 × 5 cm^3), and dried under reduced pressure. Yield: 0.060 g (94%) (Found: C, 30.0; H, 2.4; N, 4.4. C_8H_8AuN requires C, 30.5; H, 2.5; N, 4.5%). IR (KBr): ν(N–H) at 3318 and 3239; ν(C–H) at 3078, 3050 and 3030; ν(C≡C) at 2112 cm^{-1}.

$[Au(C\equiv CPh)(NH_2Bu^t)]$. Phenylethyne (0.023 cm^3, 0.204 mmol) was added dropwise to a solution of $[Au(NH_2Bu^t)_2]BF_4$ (0.088 g, 0.204 mmol) dissolved in MeCN (10 cm^{-1}) at room temperature. After stirring for 30 min the colourless solution was stored at −25 °C for *ca.* 24 h, to give colourless needles. These were subsequently filtered off and dried under reduced pressure. Yield: 0.054 g (72%) (Found: C, 39.2; H, 4.4; N, 4.5. $C_{12}H_{16}AuN$ requires C, 38.8; H, 4.3; N, 3.8%). IR(KBr): ν(N–H) at 3295, 3207 and 3135; ν(C–H) at 2965, 2924 and 2868; ν(C≡C) at 2116 cm^{-1}.

$[Au(C\equiv CBu^t)(NH_2Bu^t)]$. The method above was employed using $Bu^tC\equiv CH$ (0.025 cm^3, 0.204 mmol) and $[Au(NH_2Bu^t)_2]BF_4$ (0.088 g, 0.204 mmol). Yield: 0.032 g (44%) (Found: C, 33.8; H, 5.6; N, 3.9. $C_{10}H_{20}AuN$ requires C, 34.2; H, 5.7; N, 4.0%). IR(KBr): ν(N–H) at 3238, 3204 and 3133; ν(C–H) at 2966, 2922, 2897 and 2866; ν(C≡C) at 2106 cm^{-1}.

$[\{Au(C\equiv CBu^t)\}_6]$. *From* $[Au(NH_3)_2]BF_4$. *tert*-Butylethyne (0.06 cm^3, 0.0487 mmol) was added dropwise to $[Au(NH_3)_2]BF_4$ (0.065 g, 0.204 mmol) dissolved in predried, degassed acetonitrile (10 cm^3). After *ca.* 30 min a pale yellow solution was observed, which was then allowed to stir for 30 min, after which the volume was concentrated to *ca.* 5 cm^3 under reduced pressure to give a dark yellow precipitate. The precipitate was filtered off, dissolved in the minimum volume of hot ethanol and left in a refrigerator at 4 °C, to give pale yellow cubes after *ca.* 2 d. Yield: 0.037 g (65% based on gold) (Found: C, 25.6; H, 2.4. C_6H_9Au requires C, 25.9; H, 3.2%). IR(KBr): ν(C–H) at 2966, 2945, 2922, 2895 and 2864; ν(C≡C) at 2002, 1983 and 1964 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.2 (s, 36 H, $4Bu^t$) and 0.5 (s, 18 H, $2Bu^t$).

From $[Au(NCPh)_2]BF_4$. To a solution of $[Au(NCPh)_2]BF_4$ (0.10 g, 0.204 mmol) in acetonitrile (10 cm^3) $Bu^tC\equiv CH$ (0.06 cm^3, 0.0487 mmol) was added dropwise. After stirring for 1 h a pale yellow solution was observed. This was diluted with a large excess of ethanol (*ca.* 50 cm^3) and stored in a freezer at −25 °C for 5 d to give small yellow cubes of $[\{Au(C\equiv CBu^t)\}_6]$ which were filtered off and dried under reduced pressure. Yield: 0.015 g (27% based on gold). IR(KBr) as above.

$[Au(C\equiv CBu^t)(NH_3)]$. The complex $[\{Au(C\equiv CBu^t)\}_6]$ (0.057 g, 0.204 mmol) was dissolved in acetonitrile (15 cm^3) to give a pale yellow solution. Ammonia gas was bubbled through the solution for 15 min immediately giving a colourless solution. This was stored at −25 °C for 24 h, to give colourless needles. These were filtered off *via* a Teflon cannula and dried under reduced pressure. Yield: 0.035 g (58% based on gold) (Found: C, 24.2; H, 3.2; N, 4.4. $C_6H_{12}AuN$ requires C, 24.4; H, 4.1; N, 4.7%). IR(KBr): ν(N–H) at 3300, 3239 and 3173; ν(C–H) at 2965, 2923 and 2864; ν(C≡C) at 1963 cm^{-1}.

$[Au(C\equiv CC_6H_4Me\text{-}p)(NH_3)]$. Di-*p*-tolylethyne (0.025 g, 0.215 mmol) was added dropwise to a solution of $[Au(NH_3)_2]BF_4$ (0.065 g, 0.204 mmol) dissolved in acetonitrile (10 cm^3) to give a colourless solution. After stirring for *ca.* 15 min a colourless crystalline material appeared. Stirring was continued for 45 min, the crystalline material was filtered off *via* a Teflon cannula, washed with acetonitrile (3 × 5 cm^3) and dried under reduced pressure. Yield: 0.052 g (78% based on gold) (Found: C, 32.3; H, 2.8; N, 4.2. $C_9H_{10}AuN$ requires C, 32.8; H, 3.0; N 4.3%). IR(KBr): ν(N–R) at 3316 and 3237; ν(C=H) at 3028; ν(C=H) at 2913 and 2858; ν(C≡C) at 2101 cm^{-1}.

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