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The auration of 2-hydroxy-pyridine (2-pyridone): preparative and structural studies and a comparison with reactions of related aliphatic *O*,*N*-donors

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Abstract

In a study of the isolobal analogy between the proton H^+ and the ligand-backed gold(I) cations $[(R_3P)Au]^+$, the reaction of the mixture of 2-pyridone/2-hydroxy-pyridine tautomers with $[(Ph_3P)Au]BF_4$ has been investigated. It affords the 1:1 complex with the gold atom N-bonded to the 2-hydroxy-pyridine tautomer: $\{(Ph_3P)Au[NC_5H_4\text{-}(OH\text{-}2)]\}^+BF_4^-$, which is related to known salts with the 2-hydroxy-pyridinium cation such as $[HNC_5H_4(OH\text{-}2)]^+Cl^-$. The structure was derived from analytical and spectroscopic data and from a comparison with the salt $[(Ph_3P)Au(pyr)]BF_4$, prepared and investigated structurally as a reference compound. An analogue was also prepared with 2-dimethylamino-ethanol as a substrate, which also affords the N-bonded complex $[(Ph_3P)Au([Me_2NCH_2CH_2OH)]^+BF_4^-$, the structure of which has been determined. The OH group is not attached to the gold atom but engaged in hydrogen bonding with the counterion. By contrast, in the complex $[(Ph_3P)Au(Me_2NCH_2CH_2NMe_2)]^+BF_4^-$ synthesized similarly with tmeda and crystallized as the dichloromethane solvate, one nitrogen atom is bonded firmly to the metal atom, but the second nitrogen atom is also weakly engaged in coordinative bonding. The compound is fluxional in solution, where a site exchange is observed which is rapid on the NMR time scale. The reaction of two equivalents of $[(Ph_3P)Au]BF_4$ with an alkali 2-pyridinolate, prepared from the above tautomeric mixture and sodium metal or a potassium alkoxide, yields the diaurated product $\{N,O\text{-}[(Ph_3P)Au]_2(NC_5H_4\text{–}O\text{-}2)\}BF_4$. In the crystal structure determination of a sesqui-solvate with dichloromethane it has been shown that one gold atom is attached solely to the nitrogen atom and the other solely to the oxygen atom. The dinuclear cations are associated into cyclic dimers through head-to-tail aurophilic bonding. From the geometrical characteristics of the core unit of the cations the ligand can be assigned a 2-pyridinolate form featuring pyridine and phenolate donor sites.

Keywords: Gold complexes; Pyridine complexes; 2-Pyridone; 2-Hydroxy-pyridine

1. Introduction

For a long time the coordination chemistry of gold(I) has been largely a success story of complexes with S- and P-donor ligands, only excelled by cyanide coordination [1]. Gold thiolates AuSR and their complexes LAuSR (L = donor ligand) are the most important preparations for medical applications [2] and for traditional usage in gilding and modern surface technologies [3], including self assembly monolayers, etc. [4] although many of the precursors are not very well characterized.

The coordination chemistry of the gold(I) oxygen compounds AuOR/LAuOR is much less developed owing to preparative difficulties and a more limited stability of the products. However, it has been demonstrated that the aryloxides (phenolates) are superior in their stability to the alkoxides and that phenols may even be aurated twice to give phenoxy-bridged dinuclear cations $[ArO(AuL)_2]^+$ (Ar = aryl) [5–8].

By the same token, gold(I) complexes with nitrogen donor functions [9] are less stable than their phosphine analogues, but both anilines and in particular pyridines were found to be readily aurated [10].

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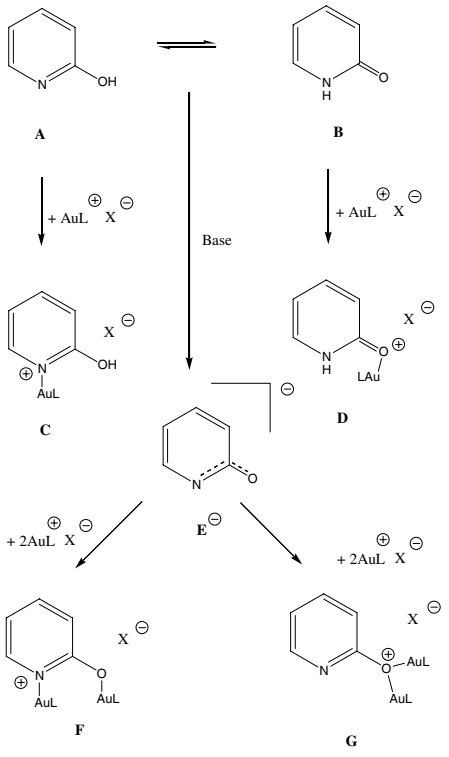
In the present study the most simple combination of phenolic and pyridine functions, 2-hydroxy-pyridine, was probed as a ligand for gold(I). The nature of the auration product was difficult to predict since the precursor molecule is an ambidentate donor which may perform either as the phenol (**A**) or as the prototropic 2-pyridone (**B**). The former would accept the metal cation at the nitrogen atom (**C**), the latter at the oxygen atom (**D**), while the corresponding anion, generated upon deprotonation (**E**), would offer two coordination sites for donor/acceptor bonding (**F**). At the phenolate function even diauration (above) could be envisaged (**G**).



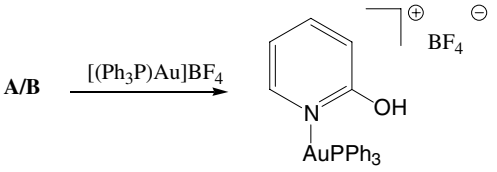
For several decades, there has been a controversy about the true nature of 2-hydroxy-pyridine/2-pyridone [11] in the crystal, in solution and in the gas phase. An early crystal structure determination at room temperature (1953) has shown that in the only modification known to date (orthorhombic, space group $P2_12_12_1, Z = 4$) the monomeric units appear to be in the 2-pyridone state, but are associated via intermolecular hydrogen bonds (O–H–N) into strings [12]. This structure has subsequently been redetermined and confirmed at least twice, including studies at low temperature [13,14]. In solution, the title compound is a mixture of both tautomers (**A/B**) with the relative abundance being a function of the polarity of the solvent, the concentration and the temperature. The monomers can also be associated into dimers via hydrogen bonds [11,15]. Finally, in the gas phase, the 2-pyridone form appears to be the dominant species according to a wealth of spectroscopic evidence [16,17]. Not all quantum-chemical studies have reached the same conclusion for the gas (or matrix) phase, since because the energy differences between the two forms are extremely small, slight variations in the parameters and models employed may cause the results to favour one or the other form [18–20].

The crystal structure of the protonated form (as the chloride hydrate) has also been elucidated previously [21], and the results have demonstrated a full conversion of the 2-pyridone into the hydroxy-pyridinium form [2-(HO)$C_5H_4NH]^+Cl^-$.

2. Results

2.1. Monoauration of 2-hydroxy-pyridine without action of a base

Solutions of 2-hydroxy-pyridine/2-pyridone in tetrahydrofuran/methanol are known to contain predominantly the former of the two components owing to advantages in its solvation. Treatment of these solutions with an equimolar quantity of (triphenylphosphine)gold(I) tetrafluoroborate, prepared in situ from the chloride complex and $AgBF_4$ at −78 °C, affords a colourless precipitate (Eq. (1)).



(1)

1

Evaporation of the solvents in a vacuum and extraction of the residue with dichloromethane give a colourless solution from which the product can be precipitated upon addition of dry diethylether in 73% yield (m.p. 97 °C with decomposition). The composition of the product (**1**) has been confirmed by elemental analysis.

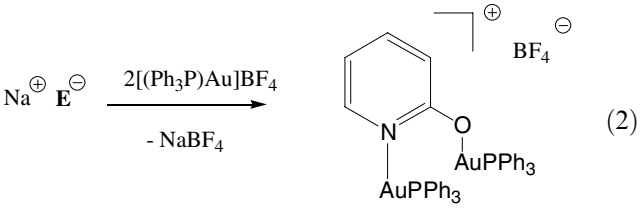
The FAB mass spectrum shows the $[(Ph_3P)Au\ x(C_5H_5NO)]^+$ cation at m/z 554.3 (in 50% relative intensity). However, the cation of highest mass is the dinuclear species $[(Ph_3P)_2Au_2(C_5H_4NO)]^+$ at m/z 1012.6 (50%) indicating the stability of the diaurated cation (below). $[(Ph_3P)_2Au]^+$ (m/z 721.5, 20%) is the product of ligand redistribution, and $[(Ph_3P)Au]^+$ is the most abundant ion at m/z 459.3 (100%). The NMR spectra of solutions in CD_2Cl_2 at 25 °C show sets of ^1H and ^{13}C resonances which can be assigned to Ph_3P and $[C_5H_4NOH]$ ligands. The latter is likely to be in the hydroxy-pyridine form because the ^{31}P signal of the Ph_3P ligand in *trans* position (30.3 ppm) appears in the same region where the resonance of the model compound $[(Ph_3P)Au(pyr)]^+BF_4^-$ is observed (30.0 ppm). The proton signal of the OH group could not be located

unambiguously, probably owing to rapid site exchange processes involving hydrogen bonds with the counterion, which has its resonances at −2.1 and −153.2 ppm for ^{11}B and ^{19}F, respectively. In the IR spectrum (KBr disc), a broad absorption with a maximum at 3051 cm^{-1} can be assigned to an OH group entertaining hydrogen bonding, but a more detailed interpretation is not justified.

2.2. Auration of 2-hydroxypyridine with the action of a base

2-Hydroxy-pyridine/2-pyridone can be converted into the phenolate ($Na^+\mathbf{E}^-$) by treatment with excess elemental sodium in tetrahydrofuran at 25 °C. After removing unreacted sodium metal the sodium salt is reacted with a solution of two equivalents of $[(Ph_3P)Au]BF_4$ in tetrahydrofuran at −78 °C. After evaporation of the solvent in a vacuum the white suspension leaves a colourless residue from which the product can be extracted with dichloromethane. Addition of *n*-pentane leads to the precipitation of a crystalline material in 31% yield (**2**, m.p. 132–134 °C).

The same product (**2**) can be obtained in a comparable yield using potassium methanolate in methanol as a base for the 2-hydroxy-pyridine.



(2)

2

The composition of the compound is confirmed by elemental analysis and the mass spectrum (FAB) which features the parent cation at m/z 1012.6 in 35% intensity relative to $[(Ph_3P)Au]^+$ (100%). The monoaurated cation appears at m/z 554.3 (10%) and the cation $[(Ph_3P)_2Au]^+$ at 721.5 (50%).

The ^1H and ^{13}C NMR spectra of **2** (in CD_2Cl_2 at 25 °C) show resonances which are very similar in their chemical shifts and coupling constants to those of compound **1** (Section 3) suggesting a similar coordination mode. In particular, one of the two ^{31}P signals of **2** (at 30.6 ppm) is almost in the same position as the single signal of **1** (30.3 ppm). The presence of a second resonance (at 27.9 ppm) is proof for the inequivalence of the two $[(Ph_3P)Au]$ groups in complex **2**. These two signals broaden and reach coalescence as the temperature is raised to 40 °C, indicating the onset of a ligand scrambling process which is rapid on the NMR time scale.

Single crystals of compound **2** (from dichloromethane/*n*-pentane at −30 °C) are monoclinic, space group *Pn*, with Z = 4 formula units (**2**) and six molecules of dichloromethane in the unit cell. There are two independent dinuclear formula units (**2**) in the asymmetric unit which are linked into tetranuclear dimers through aurophilic contacts [21]: Au1–Au4 3.2154(3), Au2–Au3 3.2780(3) Å (Fig. 1).

The structures of the two monomers (Fig. 2) are very similar and differ only in their conformation, i.e. in the dihedral angles determining the rotation of the Ph_3P propellers about the Au–P axes and the orientation of the O–Au–P vectors relative to the corresponding pyridinolate planes. Au2–O1–C1–N1: 144.4(4)°; Au4–O2–C10–N2: −154.5(4)°. The differences are best illustrated by a superposition as shown in Fig. 3. The coordination at each of the four gold atoms is very close to linear and the angles at O1 and O2 are similar at 122.7(2)° and 123.4(4)°, respectively.

The tetrafluoroborate anions and the solvent molecules reside in channels between the large dications, where no sub-van-der-Waals contacts are discernible.

Each nitrogen and oxygen atom of the pyridinolate ligands is coordinated strictly to only one gold atom. The Au–N distances [2.076(5) and 2.098(6) Å] are only slightly longer than the Au–O distances [2.059(4) and 2.055(5) Å], as expected from a smaller covalent radius of oxygen as compared to nitrogen. All four bonds can be considered strong donor/acceptor bonds which indicates that the 2-pyridinolate ligand is an efficient difunctional donor for gold(I). Nitrogen coordination (**F**) is clearly preferred over double auration of the

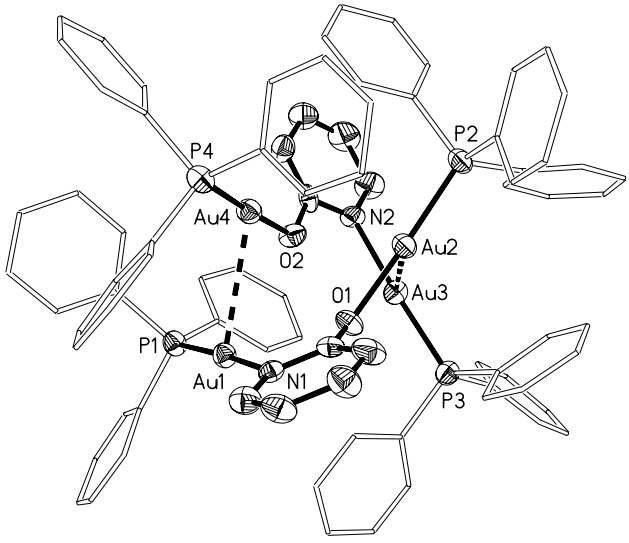


Fig. 1. Dimeric cations in the structure of compound $\mathbf{2} \times \mathbf{1.5\ CH_2Cl_2}$ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1–N1 2.076(5), Au1–P1 2.238(2), Au2–O1 2.059(4), Au2–P2 2.214(2), Au3–N2 2.098(6), Au3–P3 2.236(2), Au4–O2 2.055(5), Au4–P4 2.218(2), Au1...Au4 3.2154(3), Au2...Au3 3.2780(3); N1–Au1–P1 176.7(2), O1–Au2–P2 177.0(1), N2–Au3–P3 174.7(2), O2–Au4–P4 177.6(2).

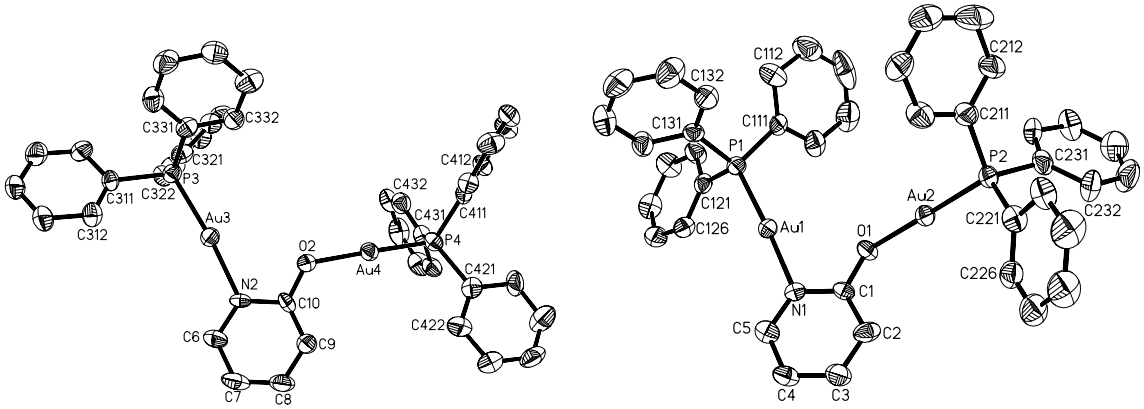


Fig. 2. Crystallographically independent cations of **2** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity).

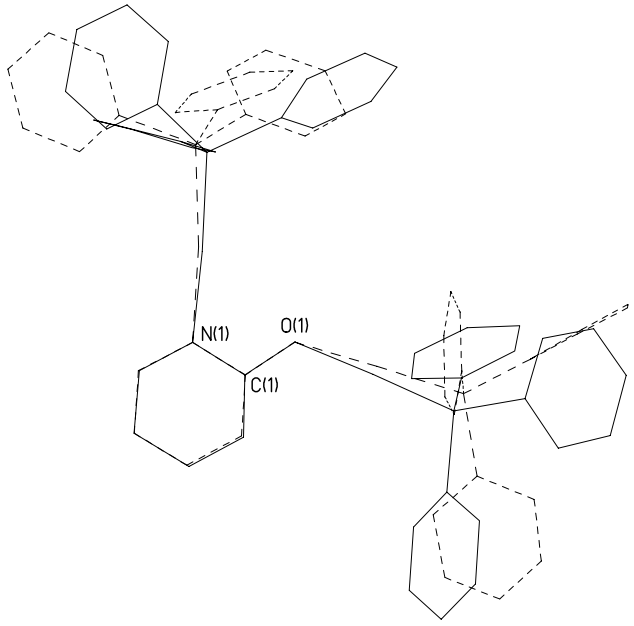
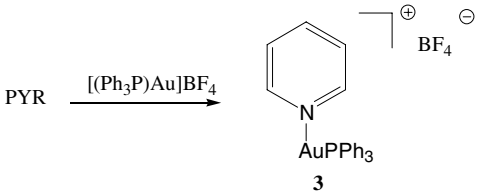


Fig. 3. Superposition of the two independent cations of **2**.

phenolate function (**G**) which is observed in the absence of the pyridine donor site [8].

2.3. Comparison to reference compounds

In order to provide benchmark data for the Au–N(pyr) bond of an unsubstituted pyridine *trans* to a Ph_3P ligand, the reference salt $[(Ph_3P)Au(pyr)]BF_4$ (**3**) has also been prepared following the same procedure as used for **1** and **2** (Eq. (3)), and structurally characterized by X-ray diffraction.



3 (3)

Crystals of **3** obtained from dichloromethane/*n*-pentane (monoclinic, space group $P2_1/n$; $Z = 4$) are solvate-free and contain only one cation and one anion in the asymmetric unit (Fig. 4). The Au–N distance was found to be 2.073(3) Å, very close to at least one of the bond lengths observed for **2**: 2.076(5) Å for Au1–N1. The Au–N coordination of the pyridinolate anion is therefore not significantly different from standard pyridine coordination suggesting that the pyridinolate/pyridone resonance is not grossly affecting the N donor strength. However, there is a significant difference in length between N1–C2 1.342(5) and N1–C6 1.342(5) Å for **3** and N1–C1 1.354(8) and N2–C10 1.366(8) Å in **2**, which shows the influence of the oxy/oxo group on the pyridine resonance reducing the bond order of the N–C(O) part of the ring.

At this point it is also of interest to compare the structural results obtained for the diaurated cation in **2** with those of the diprotonated cation of the chloride salt reported in the literature [21]: The 2-hydroxy-pyridinium cation has similar endocyclic dimensions and its exocyclic C–O bond [1.28(1) Å] can be classified as a standard single bond involving an sp^2-hybridized car-

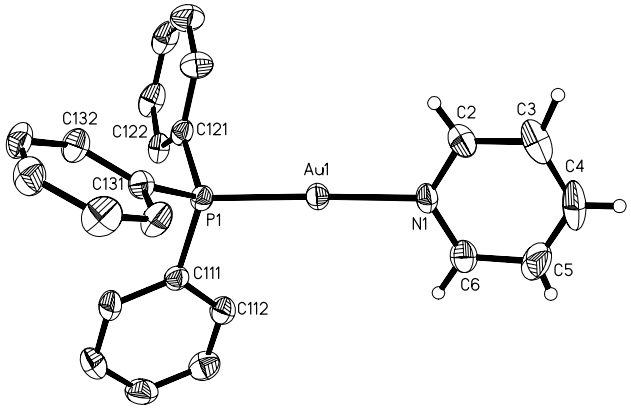
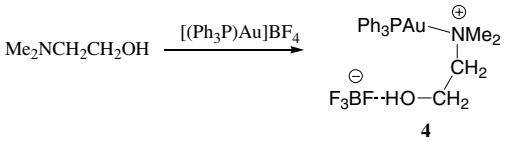


Fig. 4. Structure of the cation of compound **3** (ORTEP drawing with 50% probability ellipsoids, phenyl H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1–N1 2.073(3), Au1–P1 2.2364(8); N1–Au1–P1 178.09(8).

bon atom. The exocyclic C–O bonds in **2** are 1.326(8) and 1.302(8) Å for the two independent cations, which is not much larger considering the range of the standard deviations, and the angle H–O–C [120.7(11)°] differs by only 2° from the Au–O–C angles in the cations of complex **2**. These data indicate that protonation and auration have comparable effects on the pyridinolate ligand, as suggested by the isolobality principle [22].

2.4. Auration of 2-dimethylamino-ethanol

In order to draw a parallel to auration of the heteroaromatic 2-hydroxy-pyridine in the chemistry of saturated O/N-difunctional compounds, an analogous reaction was carried out with 2-dimethylamino-ethanol. Treatment of $[(Ph_3P)Au]BF_4$ with $Me_2NCH_2CH_2OH$ or the corresponding lithium or sodium ethanolate gave good yields of a colourless crystalline product, which was identified as the 1:1 addition compound **4** (Eq. (4)). The mass spectrum (FAB) features the cation $[Me_2N(CH_2)_2OH(AuPPh_3)]^+$ (m/z 547.6) in high intensity (55% rel. abundance), with $[(Ph_3PAu]^+$ as the most abundant ion (100%), and $[(Ph_3P)_2Au]^+$ as a product of ligand redistribution (30%).



(4)

4

The NMR spectra (in CD_2Cl_2 at 25 °C) show only one set of ligand resonances which is proof of free rotation of the aminoethanol chain in a non-cyclic array. The ^{31}P resonance at 29.3 ppm is in agreement with data for the Ph_3P ligand in a *trans* position to an amine donor at linearly two-coordinate gold [9]. OH protons are observed as a broad signal at 4.77 ppm.

Crystals of compound **4** (from dichloromethane/diethylether) are triclinic, space group $P\bar{1}$, with $Z = 2$ formula units in the unit cell. There are no solvent molecules in the crystal. The asymmetric unit contains one cation and one anion which are connected via an O–H–F(BF_3) hydrogen bond (Fig. 5).

The aminoethanol ligand is attached to the gold atom solely via its dimethylamino group. The gold atom is strictly two-coordinate with an Au–N distance of 2.112(4) Å and an angle P–Au–N of 177.39(11)°. This Au–N distance is only slightly longer than in the pyridine complexes (**2** and **3**, above), reflecting the rehybridization of the nitrogen atom from sp^2 in pyridine to sp^3 in the amine. The oxygen atom has no close intra- or inter-cationic contacts with a metal atom, even though the aminoethanol chain is in a *gauche* comformation rendering this part of the cation rather compact. The packing of cations and anions is illustrated in Fig. 6. It appears that the anions and the ammonium parts of the

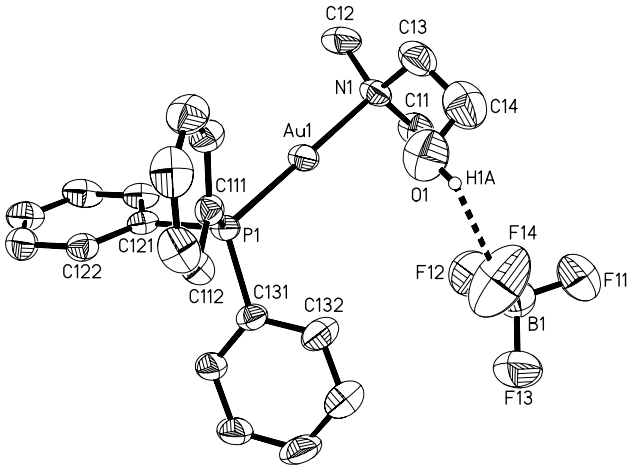


Fig. 5. Cation and anion of compound **4** (ORTEP drawing with 50% probability ellipsoids, C*H*-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1–N1 2.112(4), Au1–P1 2.227(1); N1–Au1–P1 177.4(1); O1–H1 0.840, H1…F14 2.121, O1…F14 2.760; O1–H1…F14 132.7.

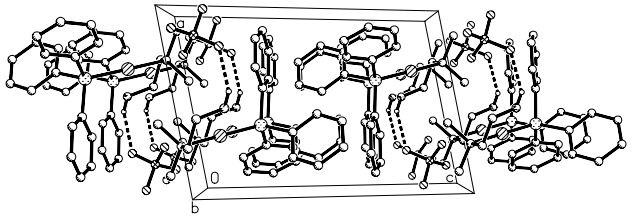


Fig. 6. View of the packing of anions and cations of compound **4** in the unit cell.

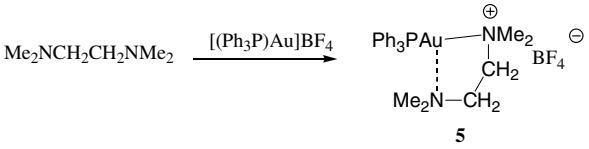
cations are held in close proximity in extended, largely ionic domains, separated by double strings of non-polar triphenylphosphine ligands. A similar structure can be proposed for compound **1**, with hydrogen bonding between a phenolic OH group and the anion.

2.5. Auration of tetramethylethylenediamine

The experiments described above have shown that gold(I) centres engaged in coordinative bonding with one Ph_3P ligand and a pyridine or a tertiary amine do not accept oxo or hydroxy donor functions available in the β-position of the primary N-ligand (**1**, **4**). Expressed in other words, there is a clear preference for the N- over the O-ligand site. In order to probe the donor/acceptor capacity of such complexes further, the coordination of the difunctional N-donor tetramethylethylenediamine (tmeda) was also investigated.

The reaction of equimolar quantities of the components $[(Ph_3P)Au]BF_4$ and tmeda in tetrahydrofuran gave good yields of a colourless crystalline product (**5**, m.p. 114 °C), which was readily identified by analytical and spectroscopic data, including FAB-MS with m/z 575.5 for M^+ (100%). In dichloromethane solution at 25 °C, the ^1H and ^{13}C NMR spectra show simple patterns

(only two resonances each for the tmeda part) suggesting either symmetrical bonding of the metal to both nitrogen atoms or unsymmetrical bonding with rapid site exchange. Lowering the temperature to −80 °C leads to line broadening but not to line splitting. The ^{31}P resonance (at 30.1 ppm) indicates strict two-coordination over the whole temperature range (v. i.).



5

(5)

Crystals of compound **5** (from dichloromethane/diethylether at −30 °C) are monoclinic, space group $P2_1$, with $Z = 2$ formula units and two dichloromethane molecules in the unit cell. Cations, anions and solvent molecules have no sub-van-der-Waals contacts. The cations show disorder of one methylene group over two positions (Fig. 7). The tmeda ligand is coordinated to the metal atom by one of its nitrogen atoms in the usual way [Au1–N1 2.133(3) Å, P1–Au1–N1 172.15(9)°], but the second nitrogen atom is also oriented towards the gold atom and approaches to an equilibrium distance Au1–N2 of 2.782(3) Å. The bending of the P1–Au1–N1 axis by ca. 8° and the folding of the tmeda ligand in its *gauche* conformation both optimize the geometry for auxiliary Au1–N2 bonding.

The results of the crystal structure determination of **5** suggest that in solution there may be rapid site exchange of the [(Ph$_3$P)Au] unit over N1 and N2 as already proposed based on the temperature-dependent NMR investigations, even though the expected signal splitting could not yet be observed at the low temperature limit.

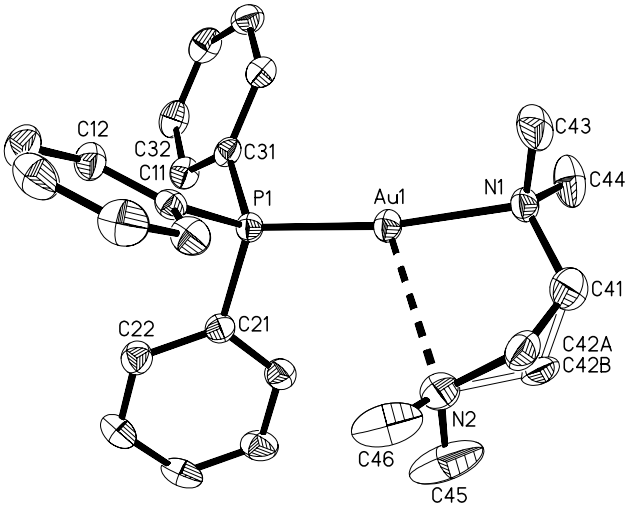


Fig. 7. Structure of the cation of compound $\mathbf{5} \times \mathbf{CH_2Cl_2}$ (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). The carbon atom C42 is disordered. Selected bond lengths [Å] and angles [°]: Au1–N1 2.133(3), Au1–P1 2.2270(8), Au1…N2 2.782(3); N1–Au1–P1 172.15(9).

It therefore appears that two-coordinate gold(I) centres have a higher affinity for a third ligand with nitrogen donor atoms as compared to oxygen donor atoms. N/O difunctional ligands are attached through the nitrogen atom only, while for N/N ligands there is strong bonding for the first, but still weak bonding for the second nitrogen atom. Considering the abundance of potential N/O donor ligands in biological systems, these results can help to guide efforts to understand the physiological function of gold(I) compounds on a molecular level.

3. Experimental

All experiments were carried out in an atmosphere of dry nitrogen. Solvents were dried and distilled under nitrogen, and glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. (Ph$_3$P)AuCl was prepared following a literature procedure [23]. All other reagents were available commercially.

*3.1. N-[(Triphenylphosphine)gold]-2-hydroxy-pyridine tetrafluoroborate (**1**)*

Solid (Ph$_3$P)AuCl (100 mg, 0.20 mmol) was added to a cooled solution of $AgBF_4$ (43 mg, 0.22 mmol) in tetrahydrofuran (5 ml) at −78 °C, and the reaction mixture was stirred for 1 h at this temperature. The supernatant was separated from the AgCl precipitate by filtration and added dropwise to a solution of 2-hydroxy-pyridine (19 mg, 0.20 mmol) in tetrahydrofuran (10 ml) kept at −78 °C. The resulting white suspension was stirred for 1 h and then evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane (10 ml), the suspension filtered and its volume reduced to 5 ml in a vacuum. The product precipitated as a coarse white solid upon addition of diethyl ether (30 ml); 81 mg (73% yield), m.p. 97 °C with decomposition. NMR (CD_2Cl_2, 25 °C), ^1H: 7.73, d, J 6.7 Hz, 1H; 6.87, d, J 8.4 Hz, 1H; 6.69, dd, 1H, all pyr; 7.42–7.68, m, 15H, Ph. $^{13}C\{^1H\}$: 141.62, 133.26, 117.54, all s, pyr; 134.53, 132.82, 129.88, 128.26, all d, J 13.1, 2.9, 12.3, and 64.5 Hz, for *o*-, *p*-, *m*-, and *i*-Ph. ^{11}B: −2.09, s. ^{19}F: −153.2, s. $^{31}P\{^1H\}$: 30.3, s. MS (FAB) m/z: 1012.6 (50%) $[M + AuPPh_3]^+$; 721.5 (20) $[(Ph_3P)_2Au]^+$; 554.3 (50) [M(cation)]$^+$; 459.3 (100) $[Ph_3PAu]^+$. *Anal.* Calc. for $C_{23}H_{20}NOAuPBF_4$ (641.17): C, 43.09; H, 3.14; N, 2.18; P, 4.83. Found: C, 44.78; H, 3.32; N, 2.09; P, 5.04%.

*3.2. N,O-Bis[(triphenylphosphine)gold]-2-pyridinolate tetrafluoroborate (**2**)*

Silver tetrafluoroborate (43 mg, 0.22 mmol) was dissolved in tetrahydrofuran (10 ml) and cooled to −78 °C.

(Triphenylphosphine)gold chloride (100 mg, 0.20 mmol) was added to this solution and the reaction mixture stirred for 1 h at −78 °C. The AgCl precipitate was removed by filtration and the filtrate added dropwise to a solution of sodium 2-pyridinolate prepared from 2-hydroxy-pyridine (10 mg, 0.10 mmol) and elemental sodium (200 mg, excess) in tetrahydrofuran (15 ml) at 25 °C and removing the excess sodium metal. The resulting white suspension was stirred for 1 h and then evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane (10 ml). After filtration the solution was reduced in volume and the product precipitated by addition of *n*-pentane. The off-white solid was recrystallized from dichloromethane by careful layering with pentane: 35 mg (31% yield), m.p. 132–134 °C with decomposition. In an alternative procedure, potassium 2-pyridinolate was prepared from 2-hydroxy-pyridine (21 mg, 0.22 mmol) and potassium methanolate (17 mg, 0.24 mmol) in methanol (10 ml) and reacted with $[(Ph_3P)Au]BF_4$ (200 mg, 0.40 mmol) in tetrahydrofuran (20 ml), with a similar yield. NMR (CD_2Cl_2, 25 °C) ^{1}H: 7.88, d, *J* 5.7 Hz, 1H, pyr; 7.35–7.80, m, 31H, Ph and pyr; 7.09, d, *J* 8.6 Hz, pyr; 6.87, dd, 1H, pyr. $^{13}C\{^1H\}$: 147.00, 142.16 and 133.21, s, pyr; 134.40, 132.80, 129.84, and 128.15, all d, for *o*-, *p*-, *m*-, and *i*-Ph, with *J* 13.5, 0.3, 11.9, and 64.5 Hz, respectively. $^{31}P\{^1H\}$: 30.6, s, 1P, PAuN; 27.9, s, 1P, PAuO. ^{11}B: −2.03, s; −1.16, s (impurity). MS (FAB) *m*/*z*: 1012.6 (35%) $[M(cation)]^+$; 721.5 (50) $[(Ph_3P)_2Au]^+$; 554.3 (10) $[M–AuPPh_3]^+$; 459.4 (100) $[Ph_3PAu]^+$. *Anal*. Calc. for $C_{41}H_{34}NOAu_2P_2BF_4$ (1099.42) C, 43.74; H, 3.62; N, 1.63; P, 5.10. Found C, 44.79; H, 3.12; N, 1.27; P, 5.63%.

3.3. Triphenylphosphine)(pyridine)gold tetrafluoroborate, (*3*)

Silver tetrafluoroborate (43 mg, 0.22 mmol) was dissolved in tetrahydrofuran (5 ml) and cooled to −78 °C. (Triphenylphosphine)gold chloride (100 mg, 0.20 mmol) was added to this solution and the reaction mixture stirred for 1 h at −78 °C. The AgCl precipitate was removed by filtration and the filtrate added dropwise to a solution of pyridine (30 mg, 0.03 ml, 0.30 mmol) in THF (5 ml). The resulting mixture was stirred for 1 h at this temperature before the solvent was removed to leave a white residue. This was extracted with 10 ml of CH_2Cl_2 and the extract filtered, reduced in volume and treated with 40 ml of diethyl ether to precipitate the product as a fine white solid; 119 mg (94%).

3.4. N-[(Triphenylphosphine)gold]-2-dimethylaminoethanol tetrafluoroborate (*4*)

Solid $(Ph_3P)AuCl$ (100 mg, 0.20 mmol) was added to a cooled solution of $AgBF_4$ (43 mg, 0.22 mmol) in tetrahydrofuran (5 ml) and the reaction mixture stirred for 1 h at −78 °C. The AgCl precipitate was filtered off and the filtrate added dropwise to a solution of 2-dimethylaminoethanol (9 mg, 0.010 ml, 0.10 mmol) in tetrahydrofuran (10 ml). The resulting off-white suspension was stirred for 2 h before reducing to dryness under vacuum. The residue was extracted with dichloromethane (5 ml), filtered to remove insoluble components and crystallized by diethyl ether vapour diffusion; colourless needles, 0.088 g (80% yield), m.p. 125 °C with decomposition. The same product was obtained in the presence of base (NaOMe or ^{n}BuLi) if moisture was not rigorously excluded. NMR (CD_2Cl_2, 25 °C), ^{1}H: 7.45–7.70, m, 15H, Ph; 4.77, bs, 1H, OH; 3.88, t, *J* 4.7 Hz, 2H, CH_2O; 3.05, t, *J* 4.7 Hz, 2H, CH_2N; 2.83, s, 6H, Me. $^{13}C\{^1H\}$: 134.52, 132.67, 129.80, and 128.20, all d, *J* 13.5, 0.5, 11.9, and 64.4 Hz, for *o*-, *p*-, *m*-, and *i*-Ph, respectively; 65.23, s, CH_2O; 58.22, s, CH_2N; 49.42, s, Me. $^{31}P\{^1H\}$: 29.3, s. MS (FAB) *m*/*z*: 721.5 (30%) $[(Ph_3P)_2Au]^+$; 547.6 (55) $[M(cation)]^+$; 459.3 (100) $[(Ph_3P)Au]^+$. *Anal*. Calc. for $C_{22}H_{26}NOPAuBF_4$ (635.20) C, 40.57; H, 4.13; N, 2.21; P, 4.88. Found C, 40.57; H, 4.24; N, 2.44; P, 4.59%.

3.5. N-[(Triphenylphosphine)gold]-tetramethylethylenediamine tetrafluoroborate (*5*)

A solution of $[(Ph_3P)Au]BF_4$ was prepared by stirring equimolar quantities of $(Ph_3P)AuCl$ (100 mg, 0.20 mmol) with $AgBF_4$ (43 mg, 0.22 mmol) in THF (5 ml) at −78 °C for 1 h and filtering the reaction mixture. This solution was added dropwise to a solution of $Me_2NCH_2CH_2NMe_2$ (excess tmeda, 0.04 ml, 31 mg, 0.30 mmol) in 5 ml of the same solvent kept at −78 °C with stirring. After 1 h the solvent was removed in a vacuum and the residue extracted with CH_2Cl_2 (5 ml). The extract was filtered and the product precipitated by addition of diethylether (20 ml). Single crystals were grown by diethylether vapour diffusion into a solution of the compound in dichloromethane; 104 mg (69% yield), m.p. 114 °C with decomposition. NMR (CD_2Cl_2, 25 °C), ^{1}H: 7.45–7.60, m, 15H, Ph; 2.79, s, 4H, CH_2; 2.51, s, 12H, Me. At −80 °C there is line broadening of the two tmeda signals. $^{13}C\{^1H\}$: 134.31, 132.72, 129.86, and 128.74, all d (*J* 14.0, 0.5, 11.9, and 63.3 Hz), for *o*-, *p*-, *m*-, and *i*- Ph, respectively; 58.75, s, CH_2; 48.56, s, Me. $^{31}P\{^1H\}$: 30.1, s. MS (FAB) *m*/*z*: 721.5 (10%) $[(Ph_3P)_2Au]^+$; 575.5 (100) $[M(cation)]^+$; 516.4 (10) $[M(cation) + Ph_3PAu]^{2+}$; 459.3 (40) $[(Ph_3P)Au]^+$. *Anal*. Calc for $C_{24}H_{31}N_2AuPBF_4$ (662.27): C, 43.53; H, 4.72; N, 4.23; P, 4.68. Found: C, 42.34; H, 4.81; N, 3.98; P, 4.40%.

3.6. Crystal structure determinations

Specimens of suitable quality and size of compounds **2**, **3**, **4** and **5** were mounted on the ends of quartz fibers

Table 1
Crystal data, data collection, and structure refinement

	$2 \times 1.5\ CH_2Cl_2$[a]	3	4	$5 \times CH_2Cl_2$
Crystal data				
Formula	$C_{42.5}H_{37}Au_2BCl_3F_4NOP_{22}$[a]	$C_{23}H_{20}AuBF_4NP$	$C_{22}H_{26}AuBF_4NOP$	$C_{25}H_{33}AuBCl_2N_2P$
M_r	1226.76[a]	625.15	635.18	747.18
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	*Pn*	$P2_1/n$	$P\bar{1}$	$P2_1$
a (Å)	14.0873(1)	9.8533(1)	9.1818(1)	10.8371(2)
b (Å)	21.7343(2)	16.6467(3)	9.6179(1)	9.4656(2)
c (Å)	15.0374(2)	13.8064(2)	14.2653(3)	14.3424(4)
α (°)	90	90	109.450(1)	90
β (°)	93.260(1)	98.619(1)	99.855(1)	102.233(1)
γ (°)	90	90	91.582(1)	90
V (Å^3)	4596.7(1)	2239.1(1)	1165.5(1)	1437.8(1)
ρ_{calc} (g cm^{-3})	1.773[a]	1.855	1.810	1.726
Z	4	4	2	2
F (0 0 0)	2348[a]	1200	616	732
μ (Mo Kα) (cm^{-1})	66.68[a]	66.85	64.25	54.01
Data collection				
T (°C)	−130	−130	−130	−130
Measured reflections	67733	72555	31246	41743
Unique reflections	17915 [$R_{int} = 0.1480$]	4952 [$R_{int} = 0.043$]	4822 [$R_{int} = 0.034$]	5823 [$R_{int} = 0.0527$]
Absorption correction	DELABS	DELABS	DELABS	DELABS
T_{min}/T_{max}	0.247/0.705	0.409/0.800	0.398/0.795	0.475/0.830
Refinement				
Refined parameters	1018	360	280	335
Final *R* values [$I > 2\sigma(I)$]				
R_1	0.0331	0.0253	0.0331	0.0237
wR_2[b]	0.0876	0.0476	0.0858	0.0591
Absolute structure parameter	0.027(4)			−0.006(6)
ρ_{fin} (max/min) (e Å^{-3})	1.421 and −1.447	0.532 and −0.645	1.814 and −2.294	1.729 and −1.689

[a] Uncorrected data.
[b] $wR_2 = \left\{ \left[\sum w(F_o^2 - F_c^2)^2 \right] / \sum [w(F_o^2)^2] \right\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0$ ($2 \times 1.5\ CH_2Cl_2$), 0 (**3**), 0.0481 (**4**), 0.0059 ($5 \times CH_2Cl_2$); $b = 0$ ($2 \times 1.5\ CH_2Cl_2$), 4.17 (**3**), 2.0 (**4**), 0.5 ($5 \times CH_2Cl_2$).

in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo Kα radiation. Intensity data were corrected for absorption effects (DELABS from PLATON). The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97). The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were either calculated and were allowed to ride on their parent atoms with fixed isotropic contributions (**2**, **4**, **5**), or were located and refined isotropically (**3**) or were included with a fixed isotropic contribution (O–*H* in **4**), respectively. Crystals of compound **2** contained some additional disordered solvent in the lattice, which was not included in the refinement but was taken care of by the 'SQUEEZE'-procedure (from PLATON). The volume occupied by the solvent is 531 Å^3, the number of electrons per unit cell deduced by 'SQUEEZE' is 40. Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions.

4. Supplementary data

Anisotropic thermal parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS-225042–225045.

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