Synthesis and Characterization of Silver(I) and Gold(I) Complexes Bearing a Pyrido-annelated \(N\)-Heterocyclic Carbene: A Rare Example of a Cocrystal Containing Two Different Gold(I) Complexes

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80\(^{th}\) birthday

The cyclohexyl-substituted imidazo[1,5-\(a\)]pyridin-2-ium hexafluorophosphate, 2a, has been prepared as precursor for the respective pyrido-annelated \(N\)-heterocyclic carbene, [(NH\(_2\))\(_2\)]\(_2\)Ag\(3\), \(3\), has been synthesized by the reaction of 2a with AgCl/KOH in dichloromethane (DCM). Unexpectedly, the reaction of 3 with (tht)AuBr yielded both (NH\(_2\))AuBr and [(NH\(_2\))Au(tht)]\(3\), which formed a 1 : 1 cocrystal (4a, b). The complexes are aggregated to infinite chains, which are governed by both \(\pi\)-\(\pi\) stacking and weak aurophilic interactions. Subsequent oxidation of the co-crystalline material with CsBr gave (NH\(_2\))AuBr\(_3\), 5. All compounds were characterized by NMR spectroscopy, mass spectrometry and elemental analysis. Additionally, compounds 2a and 5 were investigated by electronic spectroscopy: 2a behaves like a typical aromatic compound exhibiting absorption and fluorescence bands attributable to \(\pi\)-\(\pi^*\) transitions. The Au(III) complex 5 exhibits ligand-centered fluorescence at room temperature and both ligand-centered fluorescence and a weak phosphorescence at 77 K.

Key words: Silver(I), Gold(I), \(N\)-Heterocyclic Carbenes, Crystal Structure, Cocrystal

Introduction

Silver and gold complexes bearing \(N\)-heterocyclic carbenes (NHC) have been in the focus of intense studies for over a decade [1 – 8]. Due to the fact that NHC-Ag(I) complexes are versatile carbene transfer agents, they have been synthesized as stable intermediates in the course of the preparation of many other transition metal NHC complexes [9 – 11]. They are conveniently accessible by the reaction of an imidazolium salt and Ag\(_2\)O and feature a rich coordination chemistry. NHC-Au(I) complexes have been investigated due to numerous applications ranging from homogeneous catalysts for unique C–C, C–O and C–N bond-forming reactions [12 – 22] to pharmaceutical uses as anticancer, antiarthritic and antibacterial agents [23 – 31]. In addition, NHC-Au(I) and -Au(III) complexes which contain an NHC ligand with an extended \(\pi\) system feature interesting photophysical and -chemical properties [32, 33]. NHC-Au(I) complexes are usually prepared by the reaction of \((R_2S)_2AuX\) \((R_2S = Me_2S, \text{tetrahydrothiophene}; X = \text{halide})\) with a free carbene or by the ‘silver salt’ method using \((R_2S)_2AuX\) and the respective NHC-Ag complex [34].

However, the ‘silver salt’ method has a serious disadvantage: The stoichiometry of the resulting NHC-Au(I) complex cannot be controlled by the amount of the NHC-Ag(I) complex. Usually, regardless of the actual amount of the silver reagent, either a neutral or an ionic complex of the type (NHC)AuX or [(NH\(_2\))\(_2\)]\(_2\)AuX is formed. Often, the ionic form is yielded in cases where the substituent at the N atoms of the heterocycle are functionalized by heteroatoms. The polarity of the solvent also plays a role as has been proven by very elegant NMR-spectroscopic experiments [35, 36]. A further shortcoming of the method is the unknown composition of the NHC-Ag complex if no further structural information is available. This is
a critical issue as the NHC-Ag complex is frequently used merely as an intermediate and is not isolated in many cases.

In a recent publication we described this problem for the related pyrido-annelated NHC with a diisopropyl-phenyl- and a dimethyl-phenyl-substituted imidazo[1,5-α]pyridine-3-ylidene [37]: For the methyl derivative, we isolated the neutral complex (NHC)AuBr, whereas for the isopropyl derivative the ionic complex [(NHC)2Au]PF6 was obtained. In this contribution, we present the very unusual formation of a cocrystal containing the two discrete metal complexes (NHC)AuBr and [(NHC)Au(tht)]PF6 (tht = tetrahydrothiophene).

The definition of a ‘cocrystal’ is still under debate [38 – 44]. In general, it denotes a crystalline material formed by two or more different molecular entities. Hence, this definition also includes many types of compounds like hydrates, solvates and clathrates, etc. It was suggested to use ‘cocrystal’ as a synonym for a ‘multi-component molecular crystal’, a denotation which is somewhat inconvenient. However, the question is still open whether an ionic material which has been formed by proton transfer is a cocrystal, a salt or both. There are several nuances between fully protonized on one side and completely separated, neutral components which are ‘just’ connected by hydrogen bonds on the other side [45]. Nevertheless, ‘crystal engineers’ frequently use the combination of organic acids and bases as a versatile method for the preparation of new materials and call them ‘cocrystals’ even though they are actually salts [46]. There are numerous examples of such salts/cocrystals formed by the (de)prounation of active pharmaceutical ingredients to alter their bioavailability, which might be advantageous from the point of intellectual property [39].

By contrast, cocrystals composed of two or more metal complexes are rare [47 – 58]. Similar to cocrystals of purely organic compounds, weak interactions like hydrogen bonds can also be utilized to impel cocystalization of different complex molecules. Furthermore, metal atoms offer second-coordination sphere interactions or metallophilic interactions as additional driving forces for the self-organization in the solid state. Metallophilic interactions are particularly important for low-coordinate heavy metal atoms. Because metallophilic interactions reach their maximum for linearly coordinated Au(I) complexes and are in the range of the strength of hydrogen bonds, they should be ideally suited for the formation of cocrystals. Indeed, aurophilic interactions have been utilized to synthesize homo- and heterometallic clusters from two different metal complexes [59]. However, the ‘molecular entities’ are usually completely merged into the clusters. Likewise, salts containing complex cations and anions formed from neutral complexes by ligand scrambling reactions are no cocrystals in a narrow definition.

Results and Discussion

Synthesis

The synthesis of the NHC precursor 2a started with the condensation reaction of 2-pyridyl-carbaldehyde and cyclohexyl-amine to give the imine 1 [60]. Its condensation with CH3O/HCl in dry toluene yielded 2-cyclohexyl-imidazo[1,5-α]pyridine-2-ium chloride. Precipitation from aqueous solution as hexafluorophosphate gave pure 2a. If some formaldehyde remained un-dissolved in the reaction mixture before HCl was added, considerable amounts of 2b were formed. Upon cyclization, water is formed, which can hydrolyze 1. Either the imine 1 or the recovered 2-pyridyl-carbaldehyde can efficiently substitute the formaldehyde in the cyclization reaction and facilitate the formation of the side-product 2b. The ionic NHC-silver complex [(NHC)2Ag]PF6 is accessible via the reaction of in situ generated Ag2O from KOH/AgCl with 2a. Stoichiometric reaction of 2a with (tht)AuBr gives a mixture of two complexes, [(NHC)Au(tht)]PF6 and [(NHC)AuBr] (4a and 4b), from which cocrystals are obtained upon recrystallization from DCM/Et2O. Finally, the oxidation of 4a,b with CsBr3 yields (NHC)AuBr3, 5. The reaction sequence is depicted in Scheme 1.

The identity of all compounds is supported by 1H, 13C NMR spectroscopy, mass spectrometry and elemental analysis. Upon complex formation, the signal of the acidic NC(H)N proton at 9.78 ppm vanishes. In the 1H NMR spectrum of 4a,b two sets of signals in the aromatic region are partly resolved. By comparison with the known NMR data of (NHC)AuBr complexes bearing homologous imidazo-pyridine-2-y1 ligands reported just recently by us [37], the set with the sharp signals can be assigned to 4a, whereas the broad peaks are aromatic protons of 4b. The 13C resonances are shifted from 125.3 (2a) to
170.4 ppm (3). The $^{13}$C NMR signals of the carbene carbon atoms are found at 173.5 (4a), 162.6 (4b) and 121.9 ppm (5). In the ESI mass spectra of the imidazo-pyridinium salts, the dominating species are the cations with $m/z = 201$ (2a) and 278 (2b). For the silver complex the ions $[(\text{NHC})_{2}\text{Ag}]^{+}$ (507) and $[(\text{NHC})\text{Ag}]^{+}$ (307) are detected. The mass spectrum of 4a,b shows a peak representing the cation $[(\text{NHC})_{2}\text{Au}]^{+}$ (597) which results from ligand exchange reactions. The cation $[(\text{NHC})\text{Au(tht)}]^{+}$ could not be detected, presumably because of the facile dissociation of the tht ligand. The MS spectrum of 5 shows signals for the cations $[(\text{NHC})_{2}\text{Au}]^{+}$ and the bromonium ion $[(\text{NHC})\text{Au}_{2}\text{Br}]^{+}$ (875). The mass spectroscopic detection of halonium ions $[(\text{LAu})_{2}X]^{+}$ (X = Cl, Br) is common for phosphane gold(I) complexes, but is relatively rare for $\text{L} = \text{NHC}$ [61–63]. It should be noted that for neutral complexes of the form $(\text{NHC})\text{AuX}$ and $(\text{NHC})\text{AuXY}_2$ (X, Y = Cl, Br), the cation $[(\text{NHC})_{2}\text{Au}]^{+}$ is the dominant signal in the ESI mass spectra, whereas the signal for $[(\text{NHC})\text{AuBr}_2]^{+}$ is never and the one for $[(\text{NHC})\text{Au}]^{+}$ is not very often observed or very weak. The reason for the absence of an Au(III) signal is the easy reductive elimination of Br$_2$ and the high stability of the formed Au(I) species [34, 37, 62].

**Structural studies**

The molecular structures of compounds 2–4 were determined by single-crystal X-ray diffraction. Complex 2a crystallizes in the monoclinic space group $P2_1/n$ with two formula units in the asymmetric unit (Fig. 1). Despite the Coulombic repulsion, the cations are aggregated to columns via relatively short π-π interactions of about 3.3 Å. Complex 2b crystallizes in the triclinic space group $\overline{P}1$ with $Z = 2$. In both structures, the PF$_6^{-}$ anions are disordered. The bond lengths and angles are as expected.

Complex 3 crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ (Fig. 2). The Ag atom is linearly coordinated by the carbon atoms of the NHC ligands [C1–Ag1–C14 174.4(3)°]. With an angle of $\sim 11^\circ$ between the two NHC planes, the ligands are not completely coplanar. Again, π-π stacking interactions are present. The Ag–C bond lengths are 2.063(9) and 2.075(9) Å and comparable to other reported Ag–C bond lengths [64]. There are no close argentophilic contacts between the silver atoms.

Cocrystals of 4a and 4b crystallize in the monoclinic space group $C_{c}$ with $Z = 4$ (Fig. 3). The gold atoms are linearly coordinated with angles of 179.4(4) and 174.3(4)° for C1–Au1–Br1 and C14–Au2–S1, respectively. Obviously, the second ligand at the gold atom does not strongly affect the Au–C bond lengths as they are very similar [2.03(1) vs. 2.00(1) Å] and comparable to reported values [34]. The Au–S bond length [2.304(4) Å] is almost identical to the bond length found in the only published example of an NHC-Au complex bearing a tht ligand (2.304 Å) [65] but slightly shorter than in analogous phosphate complexes (2.33–2.34 Å) [61, 66–69]. The cation 4a and
Fig. 1. (a) One of the two cations in crystals of 2a and (b) of 2b; (c) aggregation of the cations in 2a via π–π stacking (ellipsoids drawn at the 50% probability level). Selected bond lengths (Å) and angles (deg) for 2a: C1–N1 1.331(4), C1–N2 1.356(4); N1–C1–N2 107.7(2), parameters of the second cation (not shown): C16–N3 1.346(4), C16–N4 1.324(4); N3–C16–N4 108.0(3); 2b: C1–N1 1.368(5), C1–N2 1.352(5); N1–C1–C14–N3 132(1).

4b are synergistically connected to linear chains by both π–π interactions and relatively long Au⋯Au contacts, the latter is indicative of rather weak aurophilic interactions [Au1⋯Au2 3.498(1), Au1⋯Au2 3.591(1) Å]. The torsion angle C1–Au1–Au2–C14 of 72.7° leads to a ‘crossed swords’ motif. The reported cocrystal [AuL2][Cl][AuCl2] (L = 2-amionopyridine) is similar to 4a,b in the sense that it is also composed of a neutral complex and a complex salt which is stabilized via cooperative action of aurophilic and π–π interactions (and N–H⋯Cl hydrogen bonds) [57]. It should be noted that to our knowledge only one example of a cocrystal with two different NHC-gold complexes is known [58].

Photophysical characterization

Compounds 2a and 5 were investigated by electronic spectroscopy. Solutions of the silver complex 3 and of the mixture 4a,b were found to be too light-sensitive, and no reproducible emission spectra could be obtained. Not unexpectedly, the spectra of 2a and 5 are very similar to the ones containing the same imidazopyridine chromophore reported by us recently [37].

The NHC precursor 2a features intense and structured absorption bands which can be attributed to π–π transitions. At room temperature the compound exhibits a broad, unstructured emission band at 367 nm. The vibronic structure is much better resolved at 77 K. The maxima in both excitation spectra (r.t. and 77 K) are superimposable with the absorption spectrum (Fig. 4, Table 1). Fig. 5 shows the electronic spectra of the Au(III) complex 5 in ethanolic solution. The high-energy absorption is structured in the UV range below 350 nm similar to that of the NHC precursor, whereas the low-energy absorption band is weak and long-tailing. The latter band can be attributed
Fig. 2. Molecular structure of the cation in crystals of 3 (ellipsoids drawn at the 50% probability level). Selected bond lengths (Å) and angles (deg): C1–Ag1 2.063(9), C14–Ag1 2.075(9), N1–C1 1.374(10), N2–C1 1.382(10), N3–C14 1.356(9), N4–C14 1.365(10); C1–Ag1–C14 174.4(3), N2–C1–N1 102.3(7), N3–C14–N4 102.7(7).

Fig. 3. Aggregation of the gold complexes in crystals of 4a,b (H atoms and PF$_6^-$ anion omitted for clarity, ellipsoids drawn at the 50% probability level). Selected bond lengths (Å) and angles (deg): Au1–C1 2.03(1), Au2–C14 2.00(1), Au1–Br1 2.389(2), Au2–S1 2.304(4), Au1–Au2 3.498(1), Au1–Au2 3.591(1); C1–Au1–Br1 179.4(4), C14–Au2–S1 174.3(4), C1–Au1–Au2–C14 65.2(5).

Fig. 4 (color online). Electronic spectra of 2a (c = $3.8 \times 10^{-5}$ M in ethanol): (a) absorption, (b) emission and (e) excitation spectra recorded at 298 K ($\lambda_{\text{exc}}$ = 280 nm, $\lambda_{\text{det}}$ = 420 nm) and (c) emission and (d) excitation spectra recorded at 77 K ($\lambda_{\text{exc}}$ = 280 nm, $\lambda_{\text{det}}$ = 420 nm).
Table 1. UV/Vis and emission spectral data of compounds 2a and 5.

<table>
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<th>Compound</th>
<th>Absorption, $\lambda_{\text{max}}$ (nm)</th>
<th>Excitation, $\lambda_{\text{max}}$ (nm)</th>
<th>Emission, $\lambda_{\text{max}}$ (nm)</th>
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<td></td>
<td>(log $\varepsilon/\text{mol}^{-1}\text{cm}^{-1}$)</td>
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<td>77 K</td>
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<tr>
<td>2a</td>
<td>226 (3.58), 233 (3.52), 241 (3.35), 260 (3.67), 271 (3.87), 281 (3.87), 298 (3.61), 310 (3.55), 323 (3.29)</td>
<td>255, 258, 260, 268, 279, 302, 314, 326</td>
<td>367 (broad)</td>
</tr>
<tr>
<td>5</td>
<td>235 (4.56), 259 (4.08), 270 (4.05), 281 (3.94), 310 (3.66), 325 (3.68), 341 (3.65)</td>
<td>275, 297, 318, 342 (sh)</td>
<td>390 (broad)</td>
</tr>
</tbody>
</table>

Fig. 5 (color online). Electronic spectra of 5: (a) absorption ($c = 6.4 \times 10^{-5} \text{ M in ethanol}$), (b) emission and (e) excitation spectra recorded at 298 K ($c = 1.0 \times 10^{-4} \text{ M in degassed ethanol}$, $\lambda_{\text{exc}} = 300 \text{ nm}$, $\lambda_{\text{det}} = 420 \text{ nm}$) and (c) emission and (d) excitation spectra recorded at 77 K ($c = 1.0 \times 10^{-4} \text{ M in ethanol glass}$, $\lambda_{\text{exc}} = 300 \text{ nm}$, $\lambda_{\text{det}} = 420 \text{ nm}$).

Conclusion

In this contribution we have presented the unexpected cocrystallization of (NHC)AuBr and [(NHC)Au(tht)]PF$_6$ (4a,b) with NHC = imidazo[1,5-$\alpha$]pyridin-3-ylidene. The aggregation of the complexes in the crystal is governed by both $\pi$-$\pi$ stacking and weak aurophilic interactions. The Au(III) complex 5 exhibits ligand-centered fluorescence at r.t. and both ligand-centered fluorescence and a weak phosphorescence at 77 K.

to $n(\text{Br}) \rightarrow 5d_{x^2-y^2}$ and $\pi(\text{Br}) \rightarrow 5d_{x^2-y^2}$ ligand-to-metal charge transfer (LMCT) states. The emission at room temperature has a maximum at 390 nm. At 77 K a second, very weak emission at lower energy evolves with a maximum centered around 550 nm. The similarity between the band shapes of 2a and 5 allows the high-energy emission to be attributed to ligand-centered fluorescence whereas the low-energy emission is ligand-centered phosphorescence. A comparable behavior is frequently found for Au(I) and Au(III) complexes bearing ligands with an extended $\pi$ chromophore [32, 37, 62, 70].
Experimental Section

General

All reactions and manipulations of air- and/or moisture-sensitive compounds were carried out in an atmosphere of dry nitrogen using standard Schlenk techniques. Toluene was dried and distilled from Na. All other solvents and reagents were commercially available and used as received.

Pyridine-2-carboxaldehyde was synthesized according to a published procedure from gold, bromine and tetrahydrothiophene [71, 72]. Pyridine-2-carboxaldehyde is commercially available and used as received.

Elemental analyses were carried out by the Institute of Chemical Technology of Organic Materials at the University Linz. NMR spectra were recorded on a Bruker Avance III (300 MHz) spectrometer. 1H and 13C shifts are reported in ppm relative to Si(CH3)4 and are referred internally with respect to the residual signal of the deuterated solvent. Mass spectra were collected on a Finnigan LCQ DecaXPias ion trap mass spectrometer with ESI ion source.

N-Cyclohexyl-(2-pyridyl)methanimine, 1

Cyclohexylamine (6.1 mL, 53 mmol) is added to a stirred solution of pyridine-2-carboxaldehyde (5.0 mL, 53 mmol) in 10 mL toluene. Molecular sieve (4 Å) is added, and the reaction mixture is allowed to stand for several hours. The molecular sieve is separated from the reaction mixture by filtration and the solvent is removed in vacuo. For purification, the oily residue was washed with ethanol and dried in vacuo. Yield: 8.4 g (85%) of a brown oil. Analytical data are in accordance with the literature values [60]. – 1H NMR (300 MHz, CDCl3): δ[ppm] = 8.55 (d, 1H, 3JHH = 4.8 Hz), 8.32 (s, 1H), 7.91 – 7.88 (m, 1H), 7.65 (dd, 1H, 3JHH = 7.6 Hz, 4JHH = 1.3 Hz), 7.19 (ddd, 1H, 3JHH = 7.5 Hz, 3JHH = 4.9 Hz, 4JHH = 1.1 Hz), 3.26 – 3.16 (m, 1H), 1.78 – 1.45 (m, 7H), 1.37 – 1.14 (m, 3H). – 13C[1H] NMR (75 MHz, DMSO): δ[ppm] = 159.2, 154.5, 149.0, 136.2, 124.5, 120.2, 68.4, 33.8, 25.2, 24.0.

2-Cyclohexyl-imidazo[1,5-a]pyridin-2-ium hexafluorophosphate, 2a

The reaction is carried out in an atmosphere of dry nitrogen: Paraformaldehyde (1.20 g, 0.040 mol) is completely dissolved in 250 mL of hot toluene. After the addition of imine 1 (6.30 g, 0.033 mol), 4 M HCl in 1,4-dioxane (8.4 mL, 0.034 mol) is added dropwise. After stirring for 15 h at ambient temperature, the solvent is removed and the oily residue washed with diethyl ether. To remove non-reacted paraformaldehyde, the residue is dissolved in methanol and filtered. The solvent is removed under reduced pressure, and an oil is obtained. For purification the residue is dissolved in a small amount of water. A solution of KPF6 is added to precipitate a bright-orange solid, which is purified by crystallization from dichloromethane (DCM) and diethyl ether.

Yield: 2.25 g (20%). Slow gas-phase diffusion of diethyl ether into a DCM solution gives yellow crystals of 2a suitable for X-ray diffraction. – 1H NMR (300 MHz, DMSO): δ[ppm] = 9.78 (s, 1H), 8.53 (d, 1H, 3JHH = 7 Hz), 8.35 (s, 1H), 7.84 (d, 1H, 3JHH = 9 Hz), 7.30 – 7.24 (m, 1H), 7.20 – 7.15 (m, 1H), 4.66 – 4.56 (m, 1H), 2.20 – 2.16 (m, 2H), 1.91 – 1.69 (m, 5H), 1.52 – 1.24 (m, 3H). – 13C[1H] NMR (75 MHz, DMSO): δ[ppm] = 129.3, 125.4, 124.6, 124.3, 118.1, 117.3, 111.7, 60.0, 32.9, 24.6, 24.4. – MS ((+)-ESI): m/z = 201 [C13H17N2]+. – MS ((–)-ESI): m/z = 145 [PF6]–. – C13H17N2PF6 (346.26): calcld. C 45.09; H 4.95, N 8.09; found C 45.61, H 4.81, N 8.35.

2-Cyclohexyl-3-(pyridin-2-yl)imidazo[1,5-a]pyridin-2-ium hexafluorophosphate, 2b

When the formaldehyde in the above experiment is not dissolved completely, two differently shaped types of crystals are obtained upon slow gas-phase diffusion of diethyl ether into the DCM solution of the crude reaction product. X-Ray diffraction of a pale-yellow needle gives the structure of 2b, with might result from the reaction of 1 with itself or the hydrolysis product pyridine-2-carboxaldehyde. The pale-yellow needles are separated by hand under the microscope and characterized by elemental analysis. Due to some contamination by 2a, no satisfactory elemental analysis can be obtained. The ESI mass spectrum of the crude product shows peaks of both 2a and 2b with m/z = 201 [C13H17N2]+ and 278 [C18H20N3]+. The peak at m/z = 278 [C18H20N3]+ is not detectable in the ESI mass spectrum of the purified compound 2a. – MS ((+)-ESI, crude product): m/z = 201 [C13H17N2]+, 278 [C18H20N3]+, 196 [C18H20N3–C6H10]+. – MS ((–)-ESI): m/z = 145 [PF6]–. – C18H20N3PF6 (423.34): calcld. C 51.07; H 4.76, N 9.93; found C 52.68, H 5.34, N 9.01.

Bis[2-cyclohexylimidazo[1,5-a]pyridin-3-ylidine]silver(I) hexafluorophosphate, 3

In a flask covered with aluminum foil, 2a (1.50 g, 4.33 mmol) is dissolved in 10 mL of DCM. AgCl (0.94 g, 6.6 mmol) and powdered KOH (0.38 g, 6.8 mmol) are added, and a brown suspension is formed. After stirring for 3 h at ambient temperature the reaction mixture is filtered over Celite. The solvent is partially removed in vacuo, and the product is precipitated with diethyl ether. Yield: 1.29 g (91%) of a light-brown powder. Slow gas-phase diffusion of diethyl ether into a DCM solution gives colorless needles of 3 suitable for X-ray diffraction. – 1H NMR (300 MHz, DMSO): δ[ppm] = 8.64 (d, 1H, 3JHH = 7 Hz),
Compound 3 (0.47 g, 0.72 mmol) is dissolved in 10 mL DCM. To the stirred solution solid (tht)AuBr (0.5 g, 1.4 mmol) is added, whereupon a precipitation of AgBr is formed immediately. After stirring for 30 min at ambient temperature, the AgBr is filtered off and the solvent partly removed under reduced pressure. Precipitation with diethyl ether yields a light-brown powder. Yield: 0.63 g (83%). Slow gas-phase diffusion of diethyl ether into a DCM solution gives yellow needles suitable for X-ray diffraction.

$^1$H NMR (300 MHz, DMSO): $\delta$ [ppm] = 8.77 (d, 1H, $J_{HH} = 7$ Hz), 8.64–8.47 (m, broad, 1H), 8.16 (s, 1H). 8.10 (s, broad, 1H), 7.67 (d, 1H, $J_{HH} = 9$ Hz), 7.61 (d, $J_{HH} = 8$ Hz), 7.11–7.02 (m, 2H, sharp and broad signals overlap), 6.96–6.89 (m, 2H, sharp and broad signals overlap), 4.87–4.76 (m, 1H), 4.70–4.62 (m, broad, 1H), 2.19–1.16 (m, 18H), 1.74–1.70 (m, 2H), 1.53–1.41 (m, 4H), 1.32–1.23 (m, 4H). $^1$C $^1$H NMR (75 MHz, DMSO): $\delta$ [ppm] = 173.5, 162.6, 130.0, 129.7, 127.3, 126.7, 123.4, 123.3, 118.0, 114.9, 110.4, 109.8, 61.9, 61.8, 33.8, 33.5, 30.5, 25.2, 25.0, 24.8, 24.5. – MS (ESI): m/z = 597 [C$_{26}$H$_{32}$NaAu]$^+$, 515 [C$_{26}$H$_{32}$NaAu-C$_6$H$_6$]$^+$, – MS (ESI): m/z = 145 [PF$_6$]$^-$, – C$_{30}$H$_{40}$NaBrAu$_2$PF$_6$ (1107.54): calcd. C 32.53; H 3.64, N 5.06; found C 32.33, H 3.46, N 5.01.

$^2$Iodobromo-[2-(cyclohexyl)imidazo[1,5-a]pyridin-3-ylidene]gold(III), 5

Compound 4a,b (0.30 g, 0.27 mmol) is dissolved in 15 mL DCM and cooled with an ice bath. Solid CsBr$_3$ (0.24 g, 0.64 mmol) is added and the reaction mixture stirred for 15 min and for another 30 min at ambient temperature.

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Table 2. Crystal data, data collection and structure refinement details.

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<th>2b</th>
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<td>C$<em>{26}$H$</em>{32}$P$_2$N$_4$P</td>
<td>C$<em>{28}$H$</em>{32}$AuF$_6$N$_4$P</td>
<td>C$<em>{28}$H$</em>{40}$Au$_2$BrF$_6$N$_4$PS</td>
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<td>423.34</td>
<td>653.40</td>
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<td>$P2_1/c$</td>
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<td>11.42(4)</td>
<td>19.24(4)</td>
<td>22.40(5)</td>
</tr>
<tr>
<td>α, deg</td>
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<td>68.07(18)</td>
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<td>β, deg</td>
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<td>83.92(2)</td>
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<td>86.98(2)</td>
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<td>V, Å$^3$</td>
<td>3044.7(6)</td>
<td>942.8(10)</td>
<td>2803.4(10)</td>
<td>3381.4(9)</td>
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<tr>
<td>$\rho_{calc}$, g cm$^{-1}$</td>
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<td>1.49</td>
<td>1.55</td>
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<td>2.0</td>
<td>0.8</td>
<td>10.0</td>
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<td>18.7</td>
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<td>Independent reflections</td>
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<td>2770</td>
<td>2133</td>
<td>5006</td>
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<td>R$_{int}$</td>
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<td>0.121</td>
<td>0.145</td>
<td>0.106</td>
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<td>Reflections with I &gt; 2$\sigma$(I)</td>
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<td>2046</td>
<td>1646</td>
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<td>Absorption correction</td>
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<td>multi-scan</td>
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<tr>
<td>$\theta_{min}$/max,</td>
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<td>0.71/0.95</td>
<td>0.72/0.96</td>
<td>0.38/0.63</td>
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<tr>
<td>Restrains/reined param.</td>
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<td>0/291</td>
<td>0/343</td>
<td>2/406</td>
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<tr>
<td>R1 (I &gt; 2$\sigma$(I))</td>
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<td>0.067</td>
<td>0.038</td>
<td>0.044</td>
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<tr>
<td>wR2</td>
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<td>0.214</td>
<td>0.096</td>
<td>0.097</td>
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<tr>
<td>x (Flack)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.03(1)</td>
</tr>
<tr>
<td>Δρ$_{max}$ (max/min), e Å$^{-3}$</td>
<td>0.85/–0.59</td>
<td>0.38/–0.41</td>
<td>0.41/–0.40</td>
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<td>1017393</td>
<td>1017394</td>
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thereby, the color of the reaction mixture changes from light-brown to orange. The reaction mixture is filtered, and the solvent is partly removed under reduced pressure. Precipitation with n-pentane yields complex S as a red-brown powder. Yield: 0.32 g. (93 %), — 1H NMR (300 MHz, DMSO): \( \delta [\text{ppm}] = 8.70 (d, 1H, H_a, J_{ab} = 7 \text{ Hz}), 8.49 (s, 1H, H_e), 7.73 (d, 1H, H_d, J_{ad} = 9 \text{ Hz}), 7.18 (dd, 1H, H_c, J_{bc} = 7 \text{ Hz}, 3J_{cd} = 9 \text{ Hz}), 7.09 - 7.04 (t, 1H, H_f), 7.09 - 7.04 (t, 1H, H_g), 6.72 - 6.65 (m, 2H), 6.31 - 6.23 (m, 2H). — 13C{1}H NMR (75 MHz, DMSO): \( \delta [\text{ppm}] = 131.8, 124.8 (C_a), 124.2 (C_d), 121.9 (C_c), 118.4 (C_e), 116.7 (C_b), 113.3 (C_e), 61.7, 32.5, 24.7, 24.2 \text{ (aromatic hydrogen and carbon atoms were assigned by } 1H-1H \text{ COSY, } 1H-13C \text{ HSQC and HMBC experiments). — MS ((+)-ESI): } m/z = 597 [C_{26}H_{32}N_4Au]^+, 875 [C_{26}H_{32}N_4Au_2Br]^+. \)

— C_{13}H_{16}N_{2}AuBr_{3} (636.96): calcd. C 24.51; H 2.53, N 4.40; found C 24.82, H 2.43, N 4.41.

Crystal structure determinations

Single-crystal structure analyses were carried out on a Bruker Smart X2S diffractometer operating with MoK\( \alpha \) radiation (\( \lambda = 0.71073 \text{ Å} \)). Further crystallographic and refinement data are listed in Table 2. The structures were solved by Direct Methods (SHELXS-97) [73, 74] and refined by full-matrix least-squares on \( F^2 \) (SHELXL-97) [75, 76]. The H atoms were calculated geometrically, and a riding model was applied during the refinement process. No higher symmetry could be found for \( 4a,b \) using the program PLATON [77, 78].

CCDC 1017392 – 1017395 contain the supplementary crystallographic data for \( 2a, 2b, 3, \) and \( 4a,b \). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

Acknowledgement

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