Dalton Transactions

PAPER

Cite this: Dalton Trans., 2014, 43, 8781

Received 7th March 2014, Accepted 16th April 2014 DOI: 10.1039/c4dt00695j

www.rsc.org/dalton

Introduction

In recent years, the interest in Au(III) compounds has increased significantly. For example, Au(III) complexes can be used for silver-salt-free gold catalysis¹ or as a catalyst in oxidative coupling reactions,² and there are also several reports on luminescent Au(III) complexes.3-5 However, gold chemistry is still dominated by compounds of the oxidation state +1. Complexes of Au(III) are not particularly rare, but the number of published compounds is remarkably lower than that of their Au(1) congeners. There are several reasons for this, such as the interest in catalytically or pharmaceutically active Au(1) complexes and their unique solid-state structures and luminescence behaviour.⁶ A more trivial reason might be that Au(1) compounds are more easily accessible: they are commonly synthesized by the reaction of $(R_2S)AuX$ $(R_2S = tetrahydrothiophene, Me_2S)$ and the ligand of interest under ambient conditions. No comparable general synthon is known for Au(III) complexes. For direct preparation of Au(III) complexes bearing a hard-to-oxidize ligand (e.g., pyridines, amines), the precursor of choice is HAuCl₄ or its alkali salt. For other ligands, the standard preparation is via the respective Au(1) complex and successive

a Institute of Inorganic Chemistry, Johannes Kepler University Linz, Altenbergerstr. ${\sf Re}$

69, 4040 Linz, Austria. E-mail: uwe.monkowius@jku.at; http://www.jku.at/anorganik; Fax: +43 732 2468 9681; Tel: +43 732 2468 8814

Facile oxidation of NHC-Au(I) to NHC-Au(III) complexes by CsBr₃⁺

Margit Kriechbaum,^a Daniela Otte,^a Manuela List^b and Uwe Monkowius*^a

CsBr₃ was investigated as a new and convenient oxidant for NHC-Au(i) complexes (NHC = imidazo[1,5-a]pyridin-3-ylidene) for the preparation of the respective Au(iii) complexes. The Au(i) complexes were synthesized by the silver salt method using [(NHC)₂Ag]PF₆ and (tht)AuBr. Unexpectedly, the reactions yielded both neutral (NHC)AuBr and ionic [(NHC)₂Au]PF₆, depending on the N-substituent of the NHC ligand. Oxidation with CsBr₃ gave the complexes (NHC)AuBr₃ and [(NHC)₂AuBr₂]PF₆ in high yields and purity, which proves the suitability of this reagent. The complexes were further characterised by X-ray diffraction and electronic absorption and emission spectroscopy. The Au(i) complexes exhibit a dual emission attributable to intraligand fluorescence and phosphorescence at both room temperature and 77 K. Upon irradiation with polychromatic light (λ > 305 nm), the Au(ii) complexes are cleanly photo-reduced to the Au(i) congener.

oxidation with a halogen. Working with gaseous Cl_2 or liquid Br_2 is inconvenient, particularly when precise and small amounts are required. The only easy-to-handle halogen is I_2 , but several Au(III)-iodides are unstable and in equilibrium with their Au(II) congeners and I_2 .⁷

An attractive alternative for gaseous Cl_2 is iodobenzene dichloride, PhICl_2 , which has already been used for the synthesis of several Au(m) chlorides.⁸ This compound can be synthesized from iodobenzene and chlorine but cannot be stored for a long time.⁹ Br₂ can be 'protected' as its tribromide in CsBr₃. This substance is a solid and can be weighed conveniently under air. This reagent has in fact already been used by Bellemin-Laponnaz and Gade for the oxidation of Pt- and Rh-complexes.¹⁰ It is not commercially available, but easily accessible from CsBr and Br₂.

To demonstrate this approach for gold, we present the use of CsBr₃ for the synthesis of (NHC)AuBr₃ (NHC – N-heterocyclic carbene) from (NHC)AuBr. The NHC used was imidazo[1,5-*a*]pyridin-3-ylidene, which possesses an extended π -system. Further, we studied the basic photophysical and photochemical properties of the prepared Au(I) and Au(III) compounds.

Result and discussion

Synthesis

Synthesis of the NHC precursors 2a,b started with the condensation reaction of 2-pyridyl-carbaldehyde and the respective aniline derivative to give the imines 1a,b (Scheme 1). Their cyclisation with CH₂O–HCl in dry toluene yielded the imidazo-

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^bInstitute for Chemical Technology of Organic Materials, Johannes Kepler University Linz, Altenbergerstr. 69, 4040 Linz, Austria

[†]Electronic supplementary information (ESI) available. CCDC 985732-985740. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00695j





Scheme 1 (a) Synthesis of the NHC precursors (2a,b) and (b) of the corresponding silver and gold complexes.

[1,5-*a*]pyridin-2-ium chlorides. Precipitation from aqueous solution as hexafluorophosphate salts gave pure 2a,b. According to our standard procedure for PF₆⁻ salts, the reaction with AgCl-KOH produces the [(NHC)₂Ag]PF₆ complexes 3a,b.¹¹ Their transmetallation with (tht)AuBr (tht = tetrahydrothiophene) yielded the respective NHC-Au complexes. Interestingly, for R = Me the neutral complex (NHC)AuBr is isolated, whereas for $R = {}^{i}Pr$ the cationic complex [(NHC)₂Au]PF₆ prevails. However, the crude product 4b always contains an impurity in the form of a small amount of the neutral complex (NHC) AuBr. This result clearly demonstrates the general problem when using the silver salt method for preparing NHC-Au(I) complexes: depending on the N-substituent and solvent, but usually irrespective of the actual stoichiometry, neutral or ionic Au complexes can be formed. However, in this case the finding is somewhat surprising as the N-substituents differ only slightly and the reaction conditions are identical. The most obvious difference is the increased level of shielding of the Au⁺ atom in 4b. Steric factors can have a huge influence on the stoichiometry of gold complexes. We have previously reported on the dominance of the ionic form [L₂Au][AuCl₂] over the neutral form LAuCl bearing a very bulky phosphane ligand Ad₂BnP, which we explained by efficient shielding (and additional Au⁺–C(π) interactions).¹² Upon successive oxidation of the Au(1) complexes with CsBr₃, the corresponding NHC-Au (III) complexes 5a,b formed in high yields in a clean reaction, which proves the suitability of the preparative approach.

The identities of all compounds were proved by ¹H-, ¹³C-NMR spectroscopy and elemental analysis. Upon complex formation, the signals of the acidic NC(H)N proton vanishes (**2a**: 9.96; **2b**: 10.01 ppm). The ¹³C resonances are shifted from 134.6 (2a) and 145.0 ppm (2b) to 172.8 (3a) and 172.8 ppm (3b), respectively. The signal of the carbene carbon atom in complex 3b is split into a doublet of doublets, with a coupling between the carbon and silver atom of ${}^{1}J({}^{107/109}\text{Ag}{}^{-13}\text{C})$ of 216 Hz and 187 Hz. Complex 3a exhibits a broad doublet at 172.8 ppm, with an average silver–carbon coupling of 193 Hz. The ${}^{13}\text{C}$ -NMR signals of the carbene carbon atom for the gold complexes are found at: 164.9 (4a), 176.6 (4b), 135.1 (5a), 144.7 (5b) ppm.

Structural studies

The molecular structures of all compounds were determined by single-crystal X-ray diffraction. The diimine **1a** crystallizes in the monoclinic space group $P2_1/c$ with two molecules of the *E*-isomer in the asymmetric unit. **1b** crystallizes in the tetragonal space group $P\overline{4}2_1/c$. The asymmetric unit contains one molecule of the *E*-isomer. The N=C-C=N unit is almost planar with torsion angles of 177.51°/172.30° (N2-C6-C5-N1/N4-C20-C19-N3) (**1a**) and 176.71° (**1b**), respectively. The bond lengths and angles are as expected (Fig. S1†).

The two carbene precursors **2a** and **2b** are shown in Fig. 1. Compound **2a** crystallizes in the monoclinic space group C2/c, compound **2b**, on the other hand, in the orthorhombic space group $Pna2_1$, which indicates the influence of the substituent at the phenyl group on the arrangement in the crystal lattice. The asymmetric unit consists of one half of a formula unit. Hence, the imidazo[1,5-*a*]pyridyl moiety is disordered, and the positions labelled as N2 and C3 are occupied by both N and C atoms at a ratio of 1:1. An identical disorder has previously been found for the mesityl derivate.¹³ Also for **2b** a comparable disorder of the atoms N1 and C3 atoms was observed. In both



Fig. 1 Molecular structures of **2a** (left) and **2b** (right, ellipsoids drawn at the 50% probability level, H atoms and PF_6^- anions omitted for clarity). Selected bond lengths [Å] and angles [°] for **2a**: N1–C1 1.347(6), C1–N2 1.337(6), N2–C1–N1 108.2(5); and for **2b**: N1–C1 1.315(7), C1–N2 1.341(6), N2–C1–N1 108.5(4).



Fig. 2 Molecular structures of **3b** (left) and **4b** (right, ellipsoids drawn at the 50% probability level, H atoms and PF_6^- anions omitted for clarity). Selected bond lengths [Å] and angles [°]: **3b**: C1-Ag1 2.065(5), N1-C1 1.363(6), N2-C1 1.355(5), C1-Ag1-C1ⁱ 180, N2-C1-N1 103.2(4); **4b**: C1-Au1 2.014(5), C1ⁱ-Au1 2.014(5), C1-N1 1.362(6), C1-N2 1.350(6), C1-Au1-C1ⁱ 180.0, N1-C1-N2 104.0(4), N1-C1-Au1 131.1(3), N2-C1-Au1 124.8(3).

molecules, the phenyl group is perpendicular to the plane of the imidazo[1,5-*a*]pyridyl moiety.

The silver complex **3b** crystallizes as the cationic carbene complex with the PF_6^- counterion in the triclinic space group $P\overline{1}$. The cation has inversion symmetry, with the silver atom as the inversion centre. Hence, the silver atom is ideally linearly coordinated by two carbene carbon atoms with a C1–Ag1–C1ⁱ angle of 180° and a Ag1–C1 bond length of 2.065(5) Å (Fig. 2).

Complex **4a** crystallizes in the monoclinic space group P_{2_1}/n with one molecule of the neutral gold carbene complex in the asymmetric unit (Fig. 3). The gold atom is almost linearly coordinated by the carbene carbon and the bromine atoms with a C1–Au1–Br1 angle of 177.1(2)°. The bond lengths are 1.997(8) Å for C1–Au1 and 2.401(1) Å for Au1–Br1. Although the arrangement of the complexes seems to support dimerization of the complexes *via* aurophilic interactions, the shortest Au–Au distance [3.783(1) Å] is well over the aurophilicity limit of ~3.5 Å. Hence, the intermolecular arrangement of the complexes in the crystal is dominated by other weak interactions, particularly by $\pi\pi$ interactions among the phenyl moieties and

the imidazo-pyridyl moieties. The cationic gold carbene complex **4b** is isostructural to **3b**. The bond length C1-Au1 of 2.014(5) Å is similar to the C1-Ag1 (2.065(5) Å) bond in **3b**, illustrating the comparable radii of Ag(1) and Au(1) atoms (Fig. 2).

In the neutral Au(III) complex **5a**, the gold atom is coordinated by the carbene carbon and three bromine atoms in square-planar geometry. The C1–Au1 bond length is 2.05(1) Å. The NHC ligand induces a *trans* effect with a lengthening of the Au1–Br3 bond compared to both *cis* Au–Br bonds (2.446(1) Å vs. ~2.42 Å). These distances are very similar to reported data.^{4,7*c*,14} Due to the higher steric demand of the bromide ligands compared to the carbene carbon atom, the Br1 and Br2 are bent towards the carbene ligand [Br1–Au1–Br2 171.14 (4)°], whereas the C1–Au1–Br3 bonds are almost linear with an angle of 176.0(3)°.The angle between the coordination and the imidazo-pyridyl plane is about 80°. It is interesting to note that in several reported (NHC)Au(III)Br₃ complexes bearing both symmetrical and unsymmetrical substituted NHC ligands with small substituents at the N atom, the NHC and the Paper



Fig. 3 Molecular structure of 4a (left) and 5a (right, ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: 4a: C1– Au1 1.997(8), Au1–Br1 2.401(1), C1–N1 1.33(1), C1–N2 1.36(1), Au1–Au1ⁱ 3.783(1), C1–Au1–Br1 177.1(2), N1–C1–N2 104.7(7), N1–C1–Au1 129.9(6), N2–C1–Au1 125.4(6). 5a: Au1–C1 2.05(1), Au1–Br1 2.426(1), Au1–Br2 2.422(1), Au1–Br3 2.446(1), N2–C1 1.34(1), N1–C1 1.33(1), C1–Au1–Br3 176.0(3), Br2–Au1–Br1 171.14(4), C1–Au1–Br2 88.3(3), C1–Au1–Br1 88.7(3), N1–C1–Au1 125.7(7), N2–C1–Au1 126.5(8).

coordination planes are not perpendicular to each other and frequently feature angles of $\sim 80^{\circ}$ and even below. 4b,7c,14

Reaction of the cationic Au(I) complex 4b with CsBr₃ yielded the cationic Au(III) complex 5b. Slow gas-phase diffusion of diethyl ether into a dilute DCM solution gave small bright red platelets. The crystals were suitable for X-ray diffraction, and a structure was solved in space group $P2_1/n$. The structure refinement was somewhat complicated by solvent residue electron densities, and no satisfactory atom positions could be found for the solvent molecule. Also the PF₆⁻ counterion is highly disordered. The anisotropic refinement was not stable, and therefore the structure was refined isotropically. The structure solution verifies the cationic nature of the Au(III) complex, but a discussion of bond lengths and angles is not meaningful (see Fig. S2 in ESI[†]). When the crude product of 4b is directly reacted with CsBr3 without purification, two kinds of crystals are identified by single-crystal X-ray diffraction (see Fig. S3 ESI[†]): The majority of crystals are bright red and were identified as the cationic Au(III) complex **5b.** A second crop of very few dark red crystals appear to be the neutral Au(III) complex (NHC)AuBr₃ (5b*). However, if the pure Au(1)-complex 4b is treated with CsBr₃, the sole product is complex 5b. The structural parameters are very similar to those of complex 5a (Fig. 4).

Photophysical and photochemical characterisation

The absorption spectrum of the carbene precursor **2b** shows a structured band in the UV range with maxima at 322, 308, 297, 284, 273, and 263 nm and shoulders at 244 and 235 nm. Because of their high extinction coefficients, the absorptions can be attributed to π - π * transitions, possibly masking additional n- π * transitions. At room temperature the compound exhibits a broad emission with maxima at 332, 350, and 365 nm and a shoulder at 386 nm. As expected, the vibronic structure in the emission spectrum is much better resolved at 77 K, and in the low-energy range low-intensity peaks at 503,



Fig. 4 Molecular structure of the neutral complex 5b*. Selected bond lengths [Å] and angles [°]: Au1–C1 2.02(1), Au1–Br1 2.410(1), Au1–Br2 2.431(1), Au1–Br3 2.439(1), N2–C1 1.36(1), N1–C1 1.35(1), C1–Au1–Br3 176.0(2), Br2–Au1–Br1 176.84(3), C1–Au1–Br2 88.6(2), C1–Au1–Br1 90.7(2), N1–C1–Au1 127.0(4), N2–C1–Au1 126.8(4).

544, and 592 nm emerge – most probably due to phosphorescence. The maxima in the excitation spectra are superimposable with the absorption maxima (Fig. 5). The electronic spectra of compound 2a are very similar, as shown in Fig. S4 of the ESI† (Table 1).

Due to their light sensitivity, the silver complexes were not investigated. The low-energy onset of the absorption of the Au(I) complex is somewhat bathochromically shifted compared to the NHC precursor: **4b** starts to absorb in the UV range below 360 nm. At room temperature the emission spectrum of a degassed ethanolic solution of compound **4b** is dominated by a broad, intense emission with maxima at 375 and 394 nm and two shoulders at 354 and 423 nm. This emission is comparable to the room-temperature emission of the imidazolium salt and can be attributed to IL fluorescence. Further peaks, with very low intensity, arise in the low-energy (LE) range from 530 to 650 nm. At 77 K the low-energy emis-



Fig. 5 Top: Electronic spectra of **2b** ($c = 7.7 \times 10^{-5}$ M in ethanol): (a) absorption, (b) emission and (e) excitation spectra recorded at 298 K ($\lambda_{\text{exc.}} = 280$ nm, $\lambda_{\text{det.}} = 400$ nm) and (c) emission spectrum (asterisk: second order of excitation light) and (d) excitation spectrum recorded at 77 K ($\lambda_{\text{exc.}} = 280$ nm, $\lambda_{\text{det.}} = 400$ nm); bottom: electronic spectra of **4b** ($c = 8.5 \times 10^{-5}$ M in ethanol): (a) absorption, (b) emission and (e) excitation spectra recorded at 298 K ($\lambda_{\text{exc.}} = 300$ nm, $\lambda_{\text{det.}} = 400$ nm) and (c) emission spectrum and (d) excitation spectrum recorded at 77 K ($\lambda_{\text{exc.}} = 300$ nm, $\lambda_{\text{det.}} = 580$ nm).

sion is more intense, showing three distinct maxima at 524, 569, and 622 nm. At higher energy, emission bands of lower intensity are observed. On the basis of the structure of the LE band and the huge Stokes shift (approx. 17 200 cm⁻¹), we attribute this emission to an ³IL excited state. The long emission decay time of the LE band of 0.73 ms at 77 K further supports this interpretation (Fig. S8 ESI[†]). Complex **4a** exhibits comparable absorption, emission, and excitation spectra. The HE bands are not as structured as for **4b**, and the emission lifetime is somewhat shorter ($\tau = 0.28$ ms, see Fig. S5 and S7 ESI[†]).

In principle, the Au(III) complexes **5a,b** exhibit similar electronic spectra: Fig. 6 shows the electronic spectra of the gold (III) complex 5b in ethanolic solution. The HE absorption is structured in the UV range below 350 nm, whereas the LE absorption is weak and very broad at ~415 nm. The latter band, which is unusually strongly red-shifted and is comparable to that of K[AuBr₄], can be attributed to $n(Br) \rightarrow 5d_{x^2-y^2}$ and $\pi(Br) \rightarrow 5d_{x^2-y^2}$ ligand-to-metal charge transfer (LMCT) states.15 The overwhelming majority of compounds of type $LAuX_3$ (L = phosphanes, HNCs; X = Cl, Br) exhibit a conspicuous signal between 330 and 400 nm.^{7c,16,17} The bathochromic shift is due to the lower σ -donor ability of the NHC ligand used,¹⁸ which reduces the electron density at the gold atom and stabilizes the d-orbitals. The emission at room temperature has a maximum at 368 nm. At 77 K a second emission at lower energy evolves with maxima at 539 and 584 nm and two shoulders at 570 and 524 nm. The similarity of the bands allows the HE emission to be attributed to IL fluorescence; the LE emission is the result of an ³IL excited state. The electronic spectra of 5a are very similar (see Fig. S6).

As expected for NHC-Au(III) halides, complexes **5a,b** are light-sensitive and can be photoreduced to the Au(I) congeners.^{7c,15} The photochemical reactivity of **5b** was investigated by irradiation of an ethanolic solution with polychromatic light ($\lambda > 305$ nm). As previously reported, NHC-Au(III) bromides undergo photo-reductive elimination of Br₂ and formation of the respective NHC-Au(I) bromide (no Br₂ could be detected because of the fast oxidation of the solvent).^{7c} Fig. 7

Table 1	UV/Vis and emission	on spectroscopic data	of compounds	2-5 in ethano
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Abcomption		Emission/ λ_{max} [nm]	Excitation/ λ_{max} [nm]		
	$\lambda_{\rm max} [\rm nm] (\log \varepsilon / \rm l \ mol^{-1} \ cm^{-1})$	298 K	77 K	298 K	77 K
2a	323 (3.24), 308 (3.58), 297 (3.65), 283 (3.92), 272 (3.94), 262 (3.79), 235 (3.83)	360 (broad)	330, 346, 364, 385, 407, (503, 544, 592)	323, 308, 285, 272, 260	324, 310, 299, 281, 269, 258
4a	350 (3.30), 333 (3.51), 318 (3.61), 297 (4.03), 286 (4.07), 275 (3.92), 258 (3.76), 249 (3.79)	392	380, 400, 531, 576, 630	358, 326, 290, 271	268, 322
5a	337 (3.01), 321 (3.13), 307 (3.11), 284 (3.41), 272 (3.51), 262 (3.55), 236 (3.91)	377, 394	366, 384, 404, 433, 470, 530, 546, 576, 630	272, 325, 359	348, 327, 317, 270
2b	322 (3.26), 308 (3.58), 297 (3.67), 284 (3.96), 273 (3.97), 263 (3.83), 244 (3.58), 235 (3.74)	332, 350, 365, 386	329, 345, 362, 381, 405, 432, (506, 548, 596)	321, 307, 296, 282, 272, 260	323, 309, 297, 282, 270, 261
4b	348 (3.23), 329 (3.96), 315 (4.09), 305 (4.06), 289 (3.88), 274 (3.63), 259 (3.63)	328, 354, 375, 394, 423, 533, 573, 606, 629	350, 368, 388, 411, 436, 524, 569, 622	341, 322, 285, 272, 264, 250	382, 345, 328, 302, 310, 268
5b	338 (3.57), 321 (3.77), 308 (3.80), 286 (4.00), 275 (4.01), 265 (3.91), 232 (4.27)	331, 350, 369	347, 364, 381, 524, 539, 570, 585, 621, (638)	322, 307, 282, 270, 260, 250	356, 340, 318, 304



Fig. 6 Electronic spectra of **5b** ($c = 8.0 \times 10^{-5}$ M in ethanol): (a) absorption, (b) emission and (e) excitation spectra recorded at 298 K ($\lambda_{exc.}$ = 300 nm, $\lambda_{det.}$ = 400 nm) and (c) emission spectrum and (d) excitation spectrum recorded at 77 K ($\lambda_{exc.}$ = 310 nm, $\lambda_{det.}$ = 580 nm).



Fig. 7 Irradiation of an ethanolic solution of **5b** ($c = 9 \times 10^{-5}$ M) with polychromatic light ($\lambda > 305$ nm). The lower, black graph shows the absorption of an ethanolic solution of **4b**.

and S9[†] plot the spectral changes of the complexes **5a,b** upon irradiation for 5 minutes. Initially, the spectrum of **5b** shows low-energy bands at 337, 321, 308, 286, 274, and 264 nm, a high-energy absorption at 233 nm, and the broad LMCT absorption at ~415 nm. Photo-reductive elimination of bromine already takes place during the first seconds of irradiation, and after 5 minutes the Au(m) complex is completely photo-reduced. The absorption spectrum of the reduced species is superimposable with the spectrum of the Au(1) congener **4b**. Likewise, the broad LMCT absorption vanishes upon irradiation, which is in accordance with the colour change of the solution from yellow to colourless. Two isosbestic points at 293 and 355 nm are indicative of a clean photoreduction.¹⁹ A similar behaviour is observed upon irradiation of a methanolic solution of Au(m) compound **5a**.

Conclusion

We have demonstrated that $CsBr_3$ can be used as an easy-tohandle oxidant for NHC-Au(I) complexes (NHC = imidazo-[1,5-*a*]pyridin-3-ylidene). The gold complexes were further investigated by electronic absorption and emission spectroscopy. The Au(I) complexes exhibit a dual emission at both room temperature and 77 K that can be attributed to intraligand fluorescence and phosphorescence. In ethanolic solutions, the Au(II) complexes are cleanly photo-reduced to the Au (I) congeners upon irradiation with polychromic light.

Experimental section

General

All reactions and manipulations of air-sensitive 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. (tht)AuBr (tht = tetrahydrothiophene) was synthesized from gold, bromine and tetrahydrothiophene following a published procedure.^{20,21} Pyridine-2-carboxaldehyde is commercially available and was used as received.

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

For photophysical characterisation, spectroscopic-grade solvents were used throughout all measurements. Absorption spectra were recorded with a Varian Cary 300 double-beam spectrometer. Emission spectra at 300 and at 77 K were measured with a steady-state fluorescence spectrometer (Jobin Yvon Fluorolog 3). Before recording the emission and excitation spectra, the samples were degassed by at least three freeze-pump-thaw cycles. Luminescence lifetimes were measured using the Fluorolog's FL-1040 phosphorimeter accessory. The estimated experimental errors for the molar absorption coefficient and fluorescence lifetime are 5%.²² The irradiation experiments were performed with an HBO 100 W lamp using polychromatic light with $\lambda > 305$ nm (WG305 filter).

Single-crystal structure analyses were carried out on a Bruker Smart X2S diffractometer operating with Mo-K_{α} radiation ($\lambda = 0.71073$ Å). Further crystallographic and refinement data can be found in Tables 2 and 3. The structures were solved by direct methods (SHELXS-97)²³ and refined by full-matrix least squares on F^2 (SHELXL-97).²⁴ The H atoms were calculated geometrically, and a riding model was applied in the refinement process. The Flack parameter for the crystal structure of compound **2b** is 0.1(2). CCDC 985732–985740

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Table 2	Crystal data and	data collection	and structure	refinement	details for	compounds	1a, 2a,	4a,	5a
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Crystal data	1a	2a	4a	5a
Empirical formula	$C_{14}H_{14}N_2$	C ₁₅ H ₁₅ N ₂ PF ₆	C ₁₅ H ₁₄ AuBrN ₂	C15H14AuBr3N2
Formula weight	210.27	368.26	499.16	658.98
Crystal size (mm)	0.41 imes 0.37 imes 0.32	0.42 imes 0.26 imes 0.05	0.57 imes 0.17 imes 0.18	0.63 imes 0.24 imes 0.05
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	C2/c	$P2_1/n$	$P2_1/n$
a(Å)	10.2806 (13)	9.498 (5)	10.646 (2)	9.591 (2)
b (Å)	11.5990 (14)	17.132 (8)	10.8148 (19)	14.252 (3)
c (Å)	19.760 (2)	10.148 (5)	13.179 (3)	12.728 (3)
$\alpha(\circ)$	90	90	90	90
$\beta(\circ)$	97.596 (4)	107.178 (15)	107.979 (7)	99.907 (7)
γ (°)	90	90	90	90
$V(A^3)$	2335.6 (5)	1577.6 (13)	1443.3 (5)	1713.9 (6)
D_{calcd} (g cm ⁻¹)	1.196	1.550	2.297	2.554
Z	8	4	4	4
$\mu ({\rm mm}^{-1})$	0.07	0.24	12.95	15.57
$T(\mathbf{K})$	200	200	200	200
θ range (°)	2.0-23.1	2.4-20.7	2.5-25.0	2.2-25.0
No. of reflections measured	21 615	5480	8914	10 864
No. of independent reflections	3251	800	2539	3021
Parameters refined/restraints	293/0	120/0	174/0	192/0
R _{int}	0.055	0.104	0.065	0.095
Absorption correction	Multi scan	Multi scan	Multi scan	Multi scan
T_{\min}, T_{\max}	0.97, 0.98	0.66, 0.99	0.05, 0.42	0.04, 0.51
Largest diff. peak and hole ($e \text{ Å}^{-3}$)	0.21 / -0.19	0.25 / -0.24	3.84/-1.87	1.02 / -0.96
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0453$	$R_1 = 0.0518$	$R_1 = 0.0391$	$R_1 = 0.0412$
L — ())	$wR_2 = 0.1123$	$wR_2 = 0.1166$	$wR_2 = 0.1022$	$wR_2 = 0.0804$
R indices (all data)	$R_1 = 0.0714$	$R_1 = 0.0759$	$R_1 = 0.0499$	$R_1 = 0.0725$
	$wR_2 = 0.1282$	$wR_2 = 0.1263$	$wR_2 = 0.1105$	$wR_2 = 0.0926$
CCDC no.	985732	985734	985737	985739

Table 3 Crystal data and data collection and structure refinement details for compounds 1b, 2b, 3b, 4b, 5b*

Crystal data	1b	2b	3b	4b	5 b *
Empirical formula	$C_{18}H_{22}N_2$	C19H23N2PF6	C ₃₈ H ₄₄ N ₄ AgPF ₆	C38H44N4AuPF6	C19H22AuBr3N2
Formula weight	266.38	424.36	809.61	898.71	715.08
Crystal size (mm)	0.40 imes 0.32 imes 0.29	$0.40 \times 0.37 \times 0.13$	$0.37 \times 0.16 \times 0.14$	$0.60 \times 0.40 \times 0.05$	0.45 imes 0.44 imes 0.37
Crystal system	Tetragonal	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{4}2_1c$	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	15.3674 (11)	16.3670 (16)	8.527 (2)	8.6606 (9)	10.005(4)
b (Å)	15.3674 (11)	13.090 (2)	10.424 (3)	10.3644 (11)	13.609 (5)
<i>c</i> (Å)	13.9783 (11)	9.463 (3)	11.059 (3)	11.0776 (13)	16.219 (6)
α (°)	90	90	84.065 (8)	83.862 (4)	90
β (°)	90	90	73.767 (8)	74.229 (3)	100.229(14)
γ (°)	90	90	80.064 (9)	80.572 (4)	90
$V(Å^3)$	3301.1 (4)	2027.4 (7)	928.1 (4)	941.95 (18)	2173.2 (14)
$D_{\text{calcd}} (\text{g cm}^{-1})$	1.072	1.390	1.449	1.584	2.186
Z	8	4	1	1	4
$\mu (\mathrm{mm}^{-1})$	0.06	0.20	0.65	4.01	12.29
T (K)	200	200	200	200	300
θ range (°)	2.7-24.3	2.5 - 21.8	1.9-25.1	2.5 - 27.1	2.2 - 25.1
No. of reflections measured	34 152	27 566	17 396	75 271	23 730
No. of independent reflections	1507	2382	3254	4071	3826
Parameters refined/restraints	186/0	261/5	233/0	233/0	230/0
R _{int}	0.066	0.071	0.134	0.050	0.072
Absorption correction	Multi scan	Multi scan	Multi scan	Multi scan	Multi scan
T_{\min}, T_{\max}	0.98, 0.98	0.82, 0.97	0.80, 0.91	0.49, 0.82	0.07, 0.09
Largest diff. peak and hole (e $Å^{-3}$)	0.13 / -0.11	0.40/-0.33	0.77/-0.75	3.89/-1.05	0.93/-1.14
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0348$	$R_1 = 0.0553$	$R_1 = 0.0537$	$R_1 = 0.0375$	$R_1 = 0.0296$
	$wR_2 = 0.0851$	$wR_2 = 0.1498$	$wR_2 = 0.1100$	$wR_2 = 0.0933$	$wR_2 = 0.0619$
<i>R</i> indices (all data)	$R_1 = 0.0434$	$R_1 = 0.0642$	$R_1 = 0.0689$	$R_1 = 0.0376$	$R_1 = 0.0439$
	$wR_2 = 0.0916$	$wR_2 = 0.1576$	$wR_2 = 0.1300$	$wR_2 = 0.0935$	$wR_2 = 0.0671$
CCDC no.	985733	985735	985736	985738	985740

contain the supplementary crystallographic data for compounds **1a–2a**, **4a–5a**, **1b–4b**, and **5b***.

Caesium tribromide CsBr₃

CsBr₃ was synthesized following a somewhat vague procedure from the literature.²⁵ Caesium bromide CsBr (10.0 g, 47 mmol) was dissolved in a small amount of water (15 mL). Bromine Br₂ (6.76 g, 42 mmol, 0.9 equiv.) was added under stirring, whereupon an orange precipitate formed immediately. The reaction mixture was stirred for another 15 minutes at room temperature. The precipitate was filtered, washed with a very small amount of cold pentane and dried. Caesium tribromide was yielded as an orange, hygroscopic solid, which can be stored at 5 °C for months. Yield: 7.8 g (21 mmol, 50%).

2,6-Dimethyl-*N*-(2-pyridinylmethylene)phenylamine (1a). Although these Schiff bases were synthesized before,²⁶ we report here a simpler method for their synthesis. Under stirring, 6.5 ml (6.4 g, 0.053 mol) of 2,6-dimethylaniline were added to a solution of 5.0 ml pyridine-2-carboxaldehyde (5.6 g, 0.053 mol) in 10 ml toluene. Then a molecular sieve (4 Å) was added and the reaction mixture allowed to stand for several hours. Afterwards, the molecular sieve was separated from the reaction mixture by filtration and the solvent removed in vacuo. For purification, the oily residue was layered with ethanol, separated, and dried in vacuo. Yield: 9.0 g (81.0%) of a yellow oil. Yellow crystals suitable for X-ray diffraction were obtained from ethanol. Analytical data are in accordance with the literature.²⁵ ¹H-NMR (300 MHz, CDCl₃, δ [ppm]): 8.72 (d, 1H, ${}^{3}J_{HH}$ = 4.8 Hz), 8.37 (s, 1H, CH=N), 8.30 (d, 1H, ${}^{3}J_{HH}$ = 8 Hz), 7.83 (td, 1H ${}^{3}J_{HH}$ = 8 Hz, ${}^{4}J_{HH}$ = 1.5 Hz), 7.42 (ddd, 1H, ${}^{3}J_{\rm HH}$ = 7.6 Hz, ${}^{3}J_{\rm HH}$ = 4.8 Hz, ${}^{3}J_{\rm HH}$ = 1.2 Hz), 7.11–7.08 (m, 2H), 7.01-6.95 (m, 1H), 2.17 (s, 6H, CH₃). ¹³C-NMR (75 MHz, CDCl₃, δ [ppm]): 163.2, 154.0, 150.0, 149.2, 136.2, 127.8, 126.3, 124.9, 123.7, 120.7, 17.9.

2,6-Diisopropyl-N-(2-pyridinylmethylene)phenylamine (1b). Under stirring, 9.9 ml (9.3 g 0.053 mol) of 2,6-diisopropylaniline were added to a solution of 5.0 ml pyridine-2-carboxaldehyde (5.6 g, 0.053 mol) in 5 ml ethanol. Then a molecular sieve (4 Å) was added, and the reaction mixture was allowed to stand for several hours. Subsequently, the molecular sieve was separated from the reaction mixture and the solvent removed in vacuo. Recrystallization of the residue in ethanol yielded a yellow crystalline solid. Yield: 9.2 g (65.7%). The spectroscopic data correspond to the reported data.²⁷ ¹H-NMR (300 MHz, CDCl₃ δ [ppm]): 8.76 (d, 1H, ${}^{3}J_{HH}$ = 4.9 Hz), 8.38 (s, 1H), 8.32 (d, 1H, ${}^{3}J_{HH}$ = 7.8 Hz), 7.86 (t, 1H, ${}^{3}J_{HH}$ = 7.8 Hz, ${}^{4}J_{\rm HH}$ = 1.2 Hz), 7.42 (ddd, 1H, ${}^{3}J_{\rm HH}$ = 7.6 Hz, ${}^{3}J_{\rm HH}$ = 4.9 Hz, ${}^{4}J_{\rm HH}$ = 1.2 Hz), 7.24–7.14 (m, 3H), 3.03 (sept, 2H, ${}^{3}J_{\rm HH}$ = 6.9 Hz), 1.22 (d, 12H, ${}^{3}J_{HH}$ = 6.9 Hz). 13 C-NMR (75 MHz, DMSO, δ [ppm]): 163.2, 153.5, 149.7, 148.1, 137.2, 136.5, 126.0, 124.3, 122.9, 120.8, 27.5, 23.0.

2-(2',6'-Dimethylphenyl)imidazo[1,5-*a*]pyridin-2-ium hexafluorophosphate (2a). The reaction was carried out in an atmosphere of dry nitrogen: paraformaldehyde (1.07 g, 0.036 mol, 1.2 equiv.) was completely dissolved in 250 ml hot toluene. After adding imine 1a (6.0 g, 0.029 mol, 1 equiv),

4 M HCl in 1,4-dioxane (7.1 ml mol, 1 equiv.) was added dropwise. After stirring for 15 h at ambient temperature, the solvent was separated and the oily residue washed with diethyl ether. To remove non-reacted paraformaldehyde, the residue was dissolved in methanol and filtered. The solvent was removed under reduced pressure, and an oil was obtained. For purification the residue was dissolved in a small amount of water, and a solution of KPF₆ was added to precipitate compound 2a as a yellow solid. Yield: 2.75 g (43.6%). Slow gasphase diffusion of diethyl ether into a diluted DCM solution gave colourless crystals suitable for X-ray diffraction. ¹H-NMR (300 MHz, DMSO, δ [ppm]): 9.96 (s, 1H), 8.60 (d, 1H, ${}^{3}J_{HH}$ = 7 Hz), 8.43 (s, 1H), 7.94 (d, 2H, ${}^{3}J_{HH}$ = 9 Hz), 7.54–7.48 (m, 1H), 7.41-7.36 (m, 3H), 7.32-7.27 (m, 1H), 2.06 (s, 6H). ¹³C-NMR (75 MHz, DMSO, δ [ppm]): 134.6, 134.0, 130.8, 129.8, 128.8, 127.5, 125.3, 124.7, 118.3, 118.0, 114.4, 16.9. MS (ESI pos): m/z 223 $[C_{15}H_{15}N_2]^+$. MS (ESI neg): m/z 145 $[PF_6]^-$. Anal. Calcd for C₁₅H₁₅N₂PF₆ (368.26) C 48.92; H 4.11, N 7.61. Found: C 48.65, H 3.53, N 7.53.

2-(2',6'-Diisopropylphenyl)imidazo[1,5-a]pyridin-2-ium hexafluorophosphate (2b). Compound 2b was prepared analogously to 2a. Starting materials: 1b (9.19 g, 0.0346 mol), paraformaldehyde (1.3 g, 0.0433 mol), HCl 4 M in 1,4-dioxane (8.6 ml, g mol). Subsequently, metathesis with KPF_6 as described for 2a was performed. Yield: 6.3 g (58.4%) of an off-white powder. Slow gas-phase diffusion of diethyl ether into a diluted DCM solution gave colourless crystals suitable for X-ray diffraction. ¹H-NMR (300 MHz, DMSO, δ [ppm]): 10.01 (s, 1H), 8.61 (d, 1H, ${}^{3}J_{HH} = 7$ Hz), 8.52 (s, 1H), 7.94 (d, 1H, ${}^{3}J_{HH} = 9$ Hz), 7.70–7.65 (m, 1H), 7.51–7.48 (m, 2H,), 7.44-7.38 (m, 1H), 7.34-7.29 (m, 1H), 2.16 (sept, 2H, J = 7 Hz), 1.15–1.11 (m, 12H). ¹³C-NMR (75 MHz, DSMO, δ [ppm]): 145.0, 131.7, 130.9, 129.8, 127.9, 125.6, 124.8, 124.4, 118.3, 118.1, 115.7, 27.8, 24.0, 23.8. MS (ESI pos): m/z 279 $[C_{19}H_{23}N_2]^+$. MS (ESI neg): m/z 145 [PF₆]⁻. Anal. Calcd for C₁₉H₂₃N₂PF₆ (424.36) C 53.78; H 5.46, N 6.60. Found: C 53.62, H 5.19, N 6.48.

Chlorido-{2-(2',6'-dimethylphenyl)imidazo[1,5-a]pyridin-3ylidene}silver(1) (3a). In a flask covered with aluminium foil, 2a (1.50 g, 4.07 mmol) was dissolved in 10 ml DCM. AgCl (0.88 g, 6.14 mmol) and powdered KOH (0.35 g, 6.06 mmol) were added, forming a brown suspension. After stirring for 3 h at ambient temperature the reaction mixture was filtered over Celite. The solvent was partially removed in vacuo, and the product was precipitated with diethyl ether. Yield: 1.16 g (77.6%) of a yellow solid. ¹H-NMR (300 MHz, DMSO, δ [ppm]): 8.69 (d, 1H, ${}^{3}J_{HH}$ = 7 Hz), 7.93 (s, 1H), 7.65 (d, 1H, ${}^{3}J_{HH}$ = 9 Hz), 7.44–7.39 (m, 1H), 7.27–7.24 (m, 2H), 7.09 (dd, 1H ${}^{3}J_{HH}$ = 7 Hz, ${}^{3}J_{\rm HH}$ = 9 Hz), 6.95–6.90 (m, 1H), 1.74 (s, 6H). 13 C-NMR (125 MHz, DMSO, δ [ppm]): 172.8, 138.2, 134.2, 130.6, 129.5, 128.8, 128.5, 123.5, 118.0, 114.7, 113.7, 17.0. MS (ESI pos): m/z 551 $[C_{30}H_{28}N_4Ag]^+$, 361 $[C_{15}H_{14}N_2Ag + CH_3OH]^+$, 347 $[C_{15}H_{14}N_2Ag + H_2O]^+$, 329 $[C_{15}H_{14}N_2Ag]^+$, 223 $[C_{15}H_{15}N_2]^+$. Anal. Calcd for C30H28N4AgPF6 (697.41) C 51.67; H 4.05, N 8.03. Found: C 51.40, H 3.55, N 7.96.

Chlorido-{2-(2',6'-diisopropylphenyl)imidazo[1,5-*a*]pyridin-3ylidene}silver(ı) (3b). Compound 3b was prepared analogously to **3a**. Starting materials: **2b** (5.03 g, 12.58 mmol), AgCl (2.55 g, 17.79 mmol), KOH (1.04 g, 18.54 mmol). Yield: 2.22 g (42.9%) of a yellow powder. Slow gas-phase diffusion of diethyl ether into a dilute DCM solution gave colourless crystals of **3b** suitable for X-ray diffraction. ¹H-NMR (300 MHz, DMSO, δ [ppm]]: 8.45 (d, 1H, ${}^{3}J_{HH} = 7$ Hz), 8.06 (s, 1H,), 7.67 (d, 1H, ${}^{3}J_{HH} = 9$ Hz), 7.53–7.48 (m, 1H), 7.29–7.27 (m, 2H), 7.12 (dd, 1H ${}^{3}J_{HH} = 7$ Hz, ${}^{3}J_{HH} = 9$ Hz), 6.97–6.93 (m, 1H), 1.99 (sept, 2H, ${}^{3}J_{HH} = 7$ Hz), 1.06 (d, 6H, ${}^{3}J_{HH} = 7$ Hz), 0.82 (d, 6H, ${}^{3}J_{HH} = 7$ Hz). 13 C-NMR (75 MHz, DMSO, δ [ppm]]: 172.8, 144.7, 134.8, 130.4, 130.3, 128.1, 123.9, 123.8, 118.1, 115.5, 115.4, 115.1, 27.7, 24.5, 23.6. MS (ESI pos): *m*/z 665 [C₃₈H₄₄N₄Ag]⁺, 417 [C₁₉H₂₂N₂Ag + CH₃OH]⁺, 403 [C₁₉H₂₂N₂Ag + H₂O]⁺, 385 [C₁₉H₂₂N₂Ag]⁺. Anal. Calcd for C₃₈H₄₄N₄AgPF₆ (802.63) C 56.37; H 5.48, N 6.92. Found: C 56.29, H 5.36, N 6.93.

Bromido-{2-(2',6'-dimethylphenyl)imidazo[1,5-a]pyridin-3ylidene}gold(I) (4a). Compound 3a (0.501 g, 1.37 mmol) was dissolved in 10 ml DCM. To the stirred solution, solid (tht)AuBr (0.500 g, 1.37 mmol) was added, whereupon AgCl precipitate formed. After stirring for 30 min. at ambient temperature, the AgCl was filtered off and the solvent partly removed under reduced pressure. Precipitation with diethyl ether yielded complex 4a as a light-brown powder. Yield: 0.614 g (89.8%). Slow gas-phase diffusion of diethyl ether into a dilute DCM solution gave colourless platelets of 4a suitable for X-ray diffraction. ¹H-NMR (300 MHz, CDCl₃, δ [ppm]): 8.62 (dd, 1H, ${}^{3}J_{HH}$ = 7 Hz), 7.44 (d, 1H, ${}^{3}J_{HH}$ = 9 Hz), 7.36–7.31 (m, 1H), 7.21–7.17 (m, 3H), 7.00 (dd, 1H, ${}^{3}J_{HH} = 7$ Hz, ${}^{3}J_{HH} = 9$ Hz), 6.79 (td, 1H, ${}^{3}J_{HH}$ = 7 Hz, ${}^{4}J_{HH}$ = 1 Hz), 2.02 (s, 6 H). 13 C-NMR (75 MHz, CDCl₃, δ [ppm]): 176.6, 137.6, 134.9, 130.4, 130.1, 128.9, 128.0, 124.1, 117.7, 114.6, 111.7, 18.0. ¹H-NMR (300 MHz, DMSO, δ [ppm]): 8.61 (d, 1H, ${}^{3}J_{HH}$ = 7 Hz), 8.01 (s, 1H), 7.69 (d, 1H, ${}^{3}J_{HH}$ = 9 Hz), 7.46–7.41 (m, 1H), 7.33–7.31 (m, 2H), 7.12 (dd, 1H, ${}^{3}J_{HH} = 7$ Hz, ${}^{3}J_{HH} = 9$ Hz), 6.97 (t, 1H, ${}^{3}J_{HH} = 9$ 7 Hz), 1.98 (s, 6H). $^{13}\text{C-NMR}$ (75 MHz, DMSO, δ [ppm]): 164.9, 137.7, 134.5, 129.9, 129.8, 128.5, 127.0, 123.9, 118.3, 115.5, 113.4, 17.2. MS (ESI pos): m/z 641 $[C_{30}H_{28}N_4Au]^+$. Anal. Calcd for C₁₅H₁₄N₂AuBr (499.16) C 36.09; H 2.83, N 5.61. Found: C 36.15, H 2.66, N 5.56.

Bis{2-(2',6'-diisopropylphenyl)imidazo[1,5-a]pyridin-3-ylidene}gold(1) hexafluorophosphate (4b). Compound 3b (0.231 g, 0.55 mmol) was dissolved in 10 ml DCM. To the stirred solution, solid (tht)AuBr (0.200 g, 0.55 mmol) was added, whereupon AgCl precipitate formed. After stirring for 30 min. at ambient temperature, the AgCl was filtered off and the solvent partly removed under reduced pressure. Precipitation with diethyl ether yielded a light-brown powder. The ¹H-NMR of the crude compound is not clean; it possibly shows a mixture of ionic and neutral gold(1) compound. Dissolving the crude compound in DCM, filtering over celite, and precipitating with diethyl ether yielded the clean product (as a yellow solid), which appears to be the cationic gold(1) carbene. Yield: 0.283 g (93.1%) of a pale yellow powder. Slow gas-phase diffusion of diethyl ether into a dilute DCM solution gave yellow platelets of 4b suitable for X-ray diffraction. ¹H-NMR (300 MHz, CDCl₃, δ [ppm]): 8.11 (dd, 1H, ${}^{3}J_{HH} = 7$ Hz, ${}^{4}J_{HH} =$

0.9 Hz), 7.56–7.48 (m, 2H), 7.29–7.23 (m, 3H), 7.09 (ddd, 1H, ${}^{3}J_{\rm HH} = 9$ Hz, ${}^{3}J_{\rm HH} = 7$ Hz, ${}^{4}J_{\rm HH} = 0.7$ Hz), 6.94 (td, 1H, ${}^{3}J_{\rm HH} = 7$ Hz, ${}^{4}J_{\rm HH} = 1$ Hz), 2.07 (sept, 2 H, ${}^{3}J_{\rm HH} = 7$ Hz), 1.09 (d, 6H, ${}^{3}J_{\rm HH} = 7$ Hz), 0.97 (d, 6H, ${}^{3}J_{\rm HH} = 7$ Hz). 13 C-NMR (75 MHz, CDCl₃, δ [ppm]): 176.6, 145.7, 134.4, 131.0, 130.9, 126.7, 125.0, 124.2, 118.0, 116.2, 114.2, 28.4, 27.4, 24.3. Anal. Calcd for C₃₈H₄₄N₄AuPF₆ (898.72) C 50.79; H 4.93, N 6.23. Found: C 50.49, H 5.02, N 6.19. MS (ESI pos): m/z 753 [C₃₈H₄₄N₄Au]⁺.

Tribromido-{2-(2',6'-dimethylphenyl)imidazo[1,5-a]pyridin-3-ylidene}gold(III) (5a). Compound 4a (0.300 g, 0.60 mmol) was dissolved in 10 ml DCM and cooled with ice bath. Solid CsBr₃ (0.230 g, 0.61 mmol) was added, and the reaction mixture stirred for 15 min. on ice bath and for a further 30 min. at ambient temperature, during which the colour of the reaction mixture changed from light brown to orange. To remove any residues, the reaction mixture was passed through a filter, and the solvent was partly removed under reduced pressure. Precipitation with pentane yielded complex 5a as a rust-brown powder. Yield: 0.232 g (58.6%). Slow gas-phase diffusion of pentane into a dilute DCM solution gave red crystals of 5a suitable for X-ray diffraction. ¹H-NMR (300 MHz, DMSO, δ [ppm]): 8.82 (d, 1H, ³J_{HH} = 7 Hz), 8.45 (s, 1H), 7.84 (d, 1H, ${}^{3}J_{HH} = 9$ Hz), 7.51–7.46 (m, 1H), 7.36–7.26 (m, 3H), 7.21–7.16 (m, 1H), 2.14 (s, 6H). ¹³C-NMR (75 MHz, DMSO, δ [ppm]): 135.1, 131.4, 130.7, 128.9, 128.7, 125.7, 125.2, 124.9, 118.5, 117.2, 116.2, 18.7. MS (ESI pos): m/z 801 $[C_{30}H_{28}N_4AuBr_2]^+$, 722 $[C_{30}H_{28}N_4AuBr_1]^+$, 641 $[C_{30}H_{28}N_4Au]^+$, 301 $[C_{15}H_{14}N_2Br]^+$. Anal. Calcd for C15H14N2AuBr3 (658.97) C 27.34; H 2.14, N 4.25. Found: C 27.51, H 1.87, N 4.27.

Dibromido-bis{2-(2',6'-diisopropylphenyl)imidazo[1,5-a]pyridin-3-ylidene}gold(m) hexafluorophosphate (5b). Compound 4b (0.100 g, 0.11 mmol) was dissolved in 20 ml DCM and cooled with ice bath. Solid CsBr₃ (0.070 g, 0.19 mmol, 1.7 equiv.) was added, and the reaction mixture stirred for 15 min. on ice bath and for a further 30 min. at ambient temperature, during which the colour of the reaction mixture changed from light brown to red. To remove any residues, the reaction mixture was passed through a filter, then the solvent was partly removed under reduced pressure. Precipitation with diethyl ether yielded complex 5b as a rustbrown powder. Yield: 0.112 g (95.5%). Slow gas-phase diffusion of diethyl ether into a dilute DCM solution gave bright red crystals. ¹H-NMR (300 MHz, DMSO, δ [ppm]): 9.00 (d, 1H, ${}^{3}J_{HH} = 7$ Hz), 8.48 (s, 1H,), 7.82 (d, 1H, ${}^{3}J_{HH} = 9$ Hz), 7.62–7.57 (m, 1H), 7.35–7.21 (m, 4H), 2.17 (sept, 2H, ${}^{3}J_{HH}$ = 7 Hz), 0.95 (d, 6H, ${}^{3}J_{HH}$ = 7 Hz), 0.87 (d, 6H, ${}^{3}J_{HH}$ = 7 Hz). ¹³C-NMR (125 MHz, DMSO, δ [ppm]): 144.7, 137.7, 132.1, 131.6, 131.0, 126.2, 125.0, 124.4, 120.2, 118.5, 117.1, 28.2, 26.3, 22.2. MS (ESI pos): m/z 913 $[C_{38}H_{44}N_4AuBr_2]^+$, 834 $[C_{38}H_{44}N_4AuBr]^+$, 753 $[C_{38}H_{44}N_4Au]^+$. Anal. Calcd for C₃₈H₄₄N₄AuBr₂PF₆ (1058.53) C 43.12; H 4.19, N 5.29. Found: C 43.05, H 4.07, N 5.76.

Tribromido-{2-(2',6'-diisopropylphenyl)imidazo[1,5-*a*]pyridin-3ylidene}gold(m) (5b*). ¹H-NMR (300 MHz, DMSO, δ [ppm]): 8.83 (d, 1H, J_{HH} = 7 Hz), 8.58 (s, 1H), 7.69–7.63 (m, 1H), 7.47–7.44 (m, 4H), 7.32–7.25 (m, 1H), 2.05 (sept, 2H, ${}^{3}J_{HH} =$ 7 Hz), 1.13 (d, 6H, ${}^{3}J_{HH} =$ 7 Hz), 1.06 (d, 6H, ${}^{3}J_{HH} =$ 7 Hz).

Acknowledgements

We thank Prof. Benno Bildstein (University Innsbruck) and Dr I. Abfalter (JKU) for valuable suggestions. The authors thank Prof. G. Knör and the JKU for continuous and generous support of the experimental work. The NMR spectrometers were acquired in collaboration with the University of South Bohemia (CZ) with financial support from the European Union (EU) through the EFRE INTERREG IV ETC-AT-CZ programme (project number M00146, "RERI-uasb").

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