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Facile Oxidation of NHC-Au(I) to NHC-Au(III) Complexes by CsBr$_3$

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Abstract

CsBr$_3$ 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)$_2$Ag]PF$_6$ and (tht)AuBr. Unexpectedly, the reactions yielded both neutral (NHC)AuBr and ionic [(NHC)$_2$Au]PF$_6$, depending on the N-substituent of the NHC ligand. Oxidation with CsBr$_3$ gave the complexes (NHC)AuBr$_3$ and [(NHC)$_2$AuBr$_2$]PF$_6$ 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(III) complexes are cleanly photo-reduced to the Au(I) congener.

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 catalysis[1] or as a catalyst in oxidative coupling reactions,[2] and there are also several reports on luminescent Au(III) complexes.[3,4,5] 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(I) congeners. There are several reasons for this, such

as the interest in catalytically or pharmaceutically active Au(I) complexes and their unique solid-state structures and luminescence behaviour.[6] A more trivial reason might be that Au(I) 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 $HAuCl_4$ or its alkali salt. For other ligands, the standard preparation is via the respective Au(I) complex and successive 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(I) 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(III) chlorides.[8] This compound can be synthesized from iodobenzene and chlorine but cannot be stored for a long time.[9] Br_2 can be 'protected' as its tribromide in $CsBr_3$. 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 Br_2.

To demonstrate this approach for gold, we present the use of $CsBr_3$ for the synthesis of $(NHC)AuBr_3$ (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 CH_2O/HCl in dry toluene yielded the imidazo[1,5-a]pyridin-2-ium chlorides. Precipitation from aqueous solution as hexafluorophosphate salts gave pure **2a,b**. According to our standard procedure for PF_6^- salts, the reaction with AgCl/KOH produces the

$[(NHC)_2Ag]PF_6$ 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-Au-Br is formed, whereas for R = ^{i}Pr the cationic complex $[(NHC)_2Au]PF_6$ 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 $[L_2Au][AuCl_2]$ over the neutral form LAuCl bearing a very bulky phosphane ligand Ad_2BnP, which we explained by efficient shielding (and additional Au^+-C(π) interactions). [12] Upon successive oxidation of the Au(I) complexes with $CsBr_3$, 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 ^{1}H-, ^{13}C-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 ^{13}C 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($^{107/109}$Ag–^{13}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}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.

a)

1a: R = Me
1b: R = iPr

2a: R = Me
2b: R = iPr
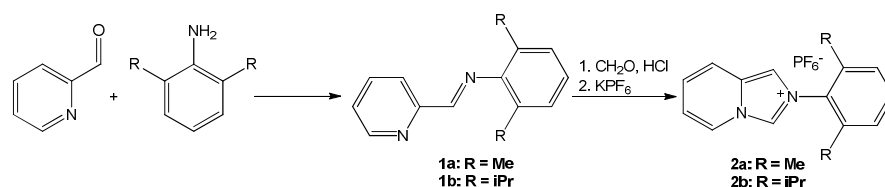
b)
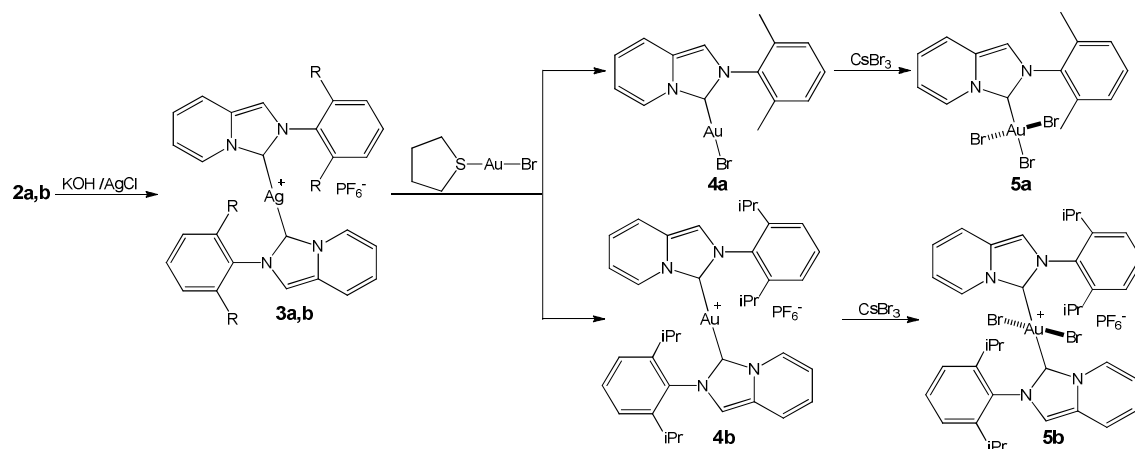
Scheme 1. (a) Synthesis of the NHC precursors (**2a,b**) and (b) of the corresponding silver and gold complexes.

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 $P\text{-}42_1/c$. 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 (Figure S1).

The two carbene precursors **2a** and **2b** are shown in Figure 1. Compound **2a** crystallizes in the monoclinic space group *C*2/*c*, compound **2b**, on the other hand, in the orthorhombic space group *Pna*2_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 molecules, the phenyl group is perpendicular to the plane of the imidazo[1,5-*a*]pyridyl moiety.
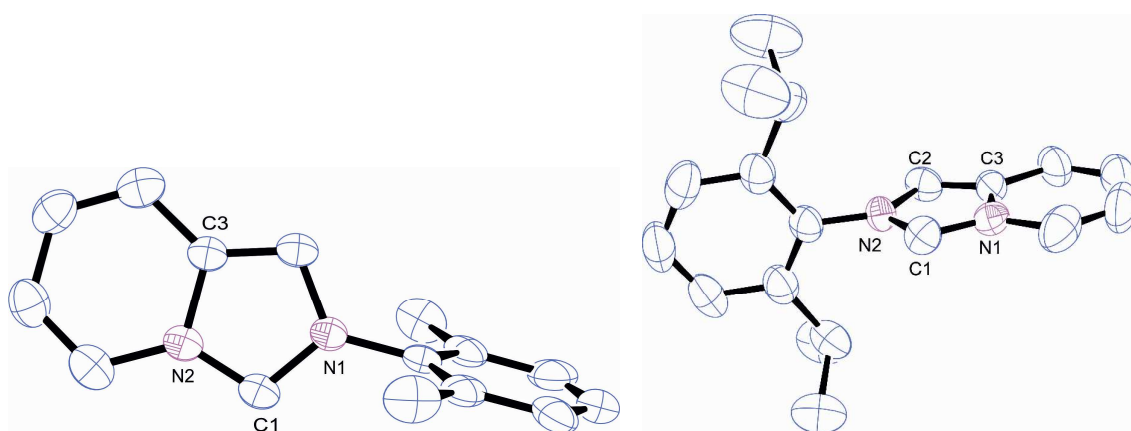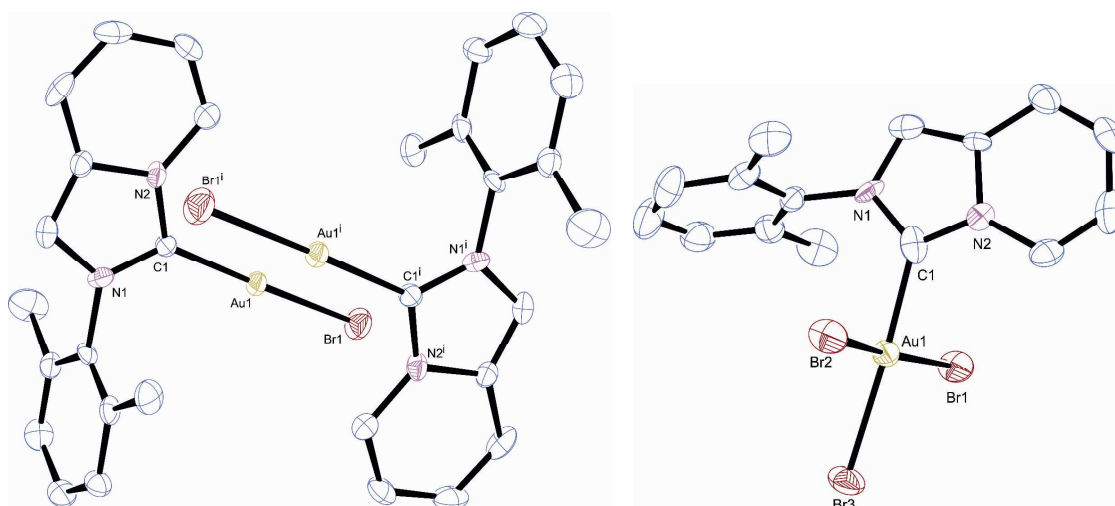
Figure 1. Molecular structures of **2a** (left) and **2b** (right, ellipsoids drawn at the 50% probability level, H atoms and PF_6^- anions omitted for clarity). Selected bond lengths [Å] and angles [°] for **2a**: N1–C1 1.347(6), C1–N2 1.337(6), N2–C1–N1 108.2(5); and for **2b**: N1–C1 1.315(7), C1–N2 1.341(6), N2–C1–N1 108.5(4).

The silver complex **3b** crystallizes as the cationic carbene complex with the PF_6^- counterion in the triclinic space group *P*-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-C1^i angle of 180° and a Ag1-C1 bond length of 2.065(5) Å (Figure 2).
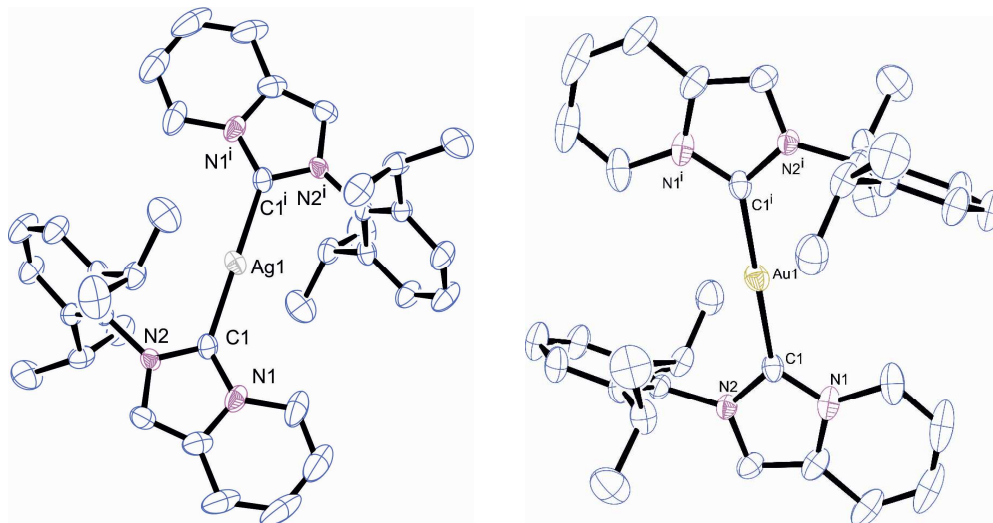
Figure 2. Molecular structures of **3b** (left) and **4b** (right, ellipsoids drawn at the 50% probability level, H atoms and PF_6^- anions omitted for clarity). Selected bond lengths [Å] and angles [°]: **3b**: C1–Ag1 2.065(5), N1–C1 1.363(6), N2–C1 1.355(5), C1–Ag1–C1^i 180, N2–C1–N1 103.2(4); **4b**: C1–Au1 2.014(5), C1^i–Au1 2.014(5), C1–N1 1.362(6), C1–N2 1.350(6), C1–Au1–C1^i 180.0, N1–C1–N2 104.0(4), N1–C1–Au1 131.1(3), N2-C1–Au1 124.8(3).

Figure 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–Au1^i 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).

Complex **4a** crystallizes in the monoclinic space group $P2_1/n$ with one molecule of the neutral gold carbene complex in the asymmetric unit (Figure 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 (Figure 3). 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 ππ 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(I) and Au(I) atoms (Figure 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 induce 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). These distances are very similar to reported data.[4,7c,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 $(NHC)Au(III)Br_3$ complexes bearing both symmetrical and unsymmetrical substituted NHC ligands with small substituents at the N atom, the NHC and the coordination planes are not perpendicular to each other and frequently feature angles of ~80° and even below.[4b,7c,14]

Reaction of the cationic Au(I)-complex **4b** with $CsBr_3$ 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 PF_6^- 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 Figure S2 in Supplementary Information). When the crude product of **4b** is directly reacted with $CsBr_3$ without purification, two kinds of crystals are identified by single-crystal X-ray diffraction (see Figure S3 Supplementary Information): The majority of crystals are bright red and were identified as the cationic gold(III) complex **5b**. A second crop of very few dark red crystals appear to be the neutral gold(III) complex $(NHC)AuBr_3$ (**5b***). However, if the pure gold(I)-complex **4b** is treated with $CsBr_3$, the sole product is complex **5b**. The structural parameters are very similar to those of complex **5a** (Figure 4).
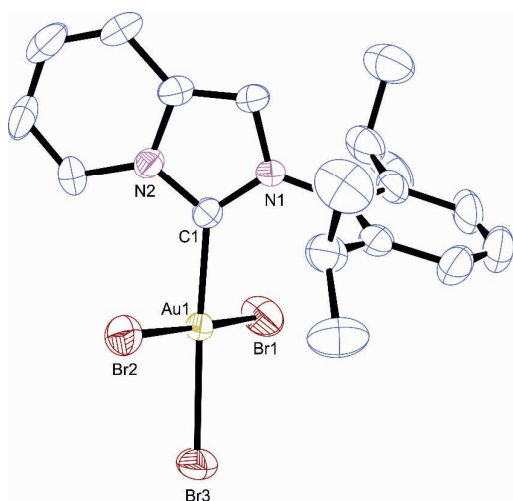

Figure 4: Molecular structure of the neutral complex **5b***. Selected bond lengths [Å] and angles [°]: Au1–C1 2.02(1), Au1–Br1 2.410(1), Au1–Br2 2.431(1), Au1–Br3 2.439(1), N2–C1 1.36(1), N1–C1 1.35(1), C1–Au1–Br3 176.0(2), Br2–Au1–Br1 176.84(3), C1–Au1–Br2 88.6(2), C1–Au1–Br1 90.7(2), N1–C1–Au1 127.0(4),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

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, 544, and 592 nm emerge – most probably due to phosphorescence. The maxima in the excitation spectra are superimposable with the absorption maxima (Figure 5). The electronic spectra of compound **2a** are very similar, as shown in Figure S4 of the Supplementary Information (Table 1).
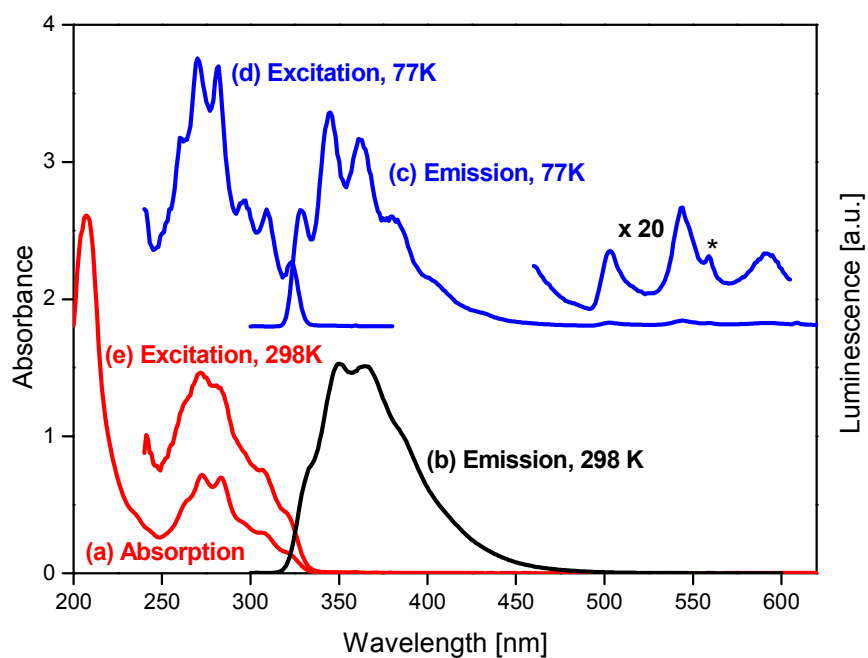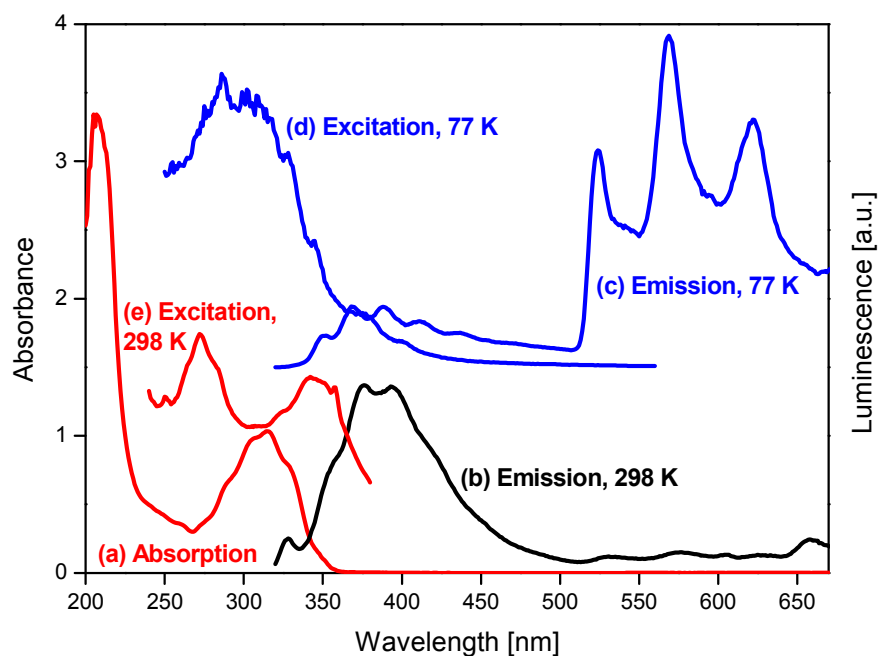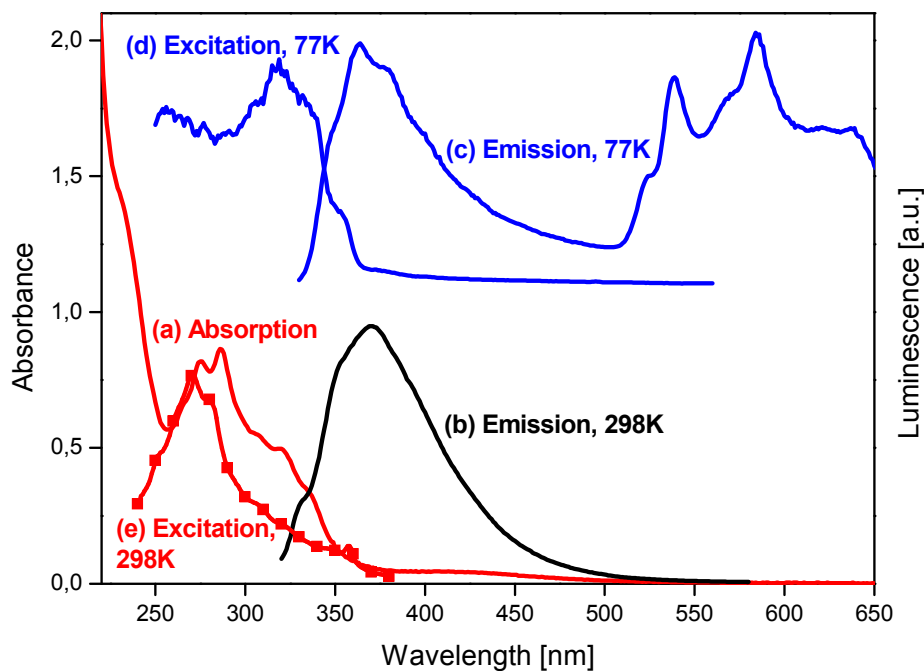
Figure 5: top: Electronic spectra of **2b** (c = 7.7 10^{-5} M in ethanol): (a) absorption, (b) emission and (e) excitation spectra recorded at 298 K ($\lambda_{exc.}$ = 280 nm, $\lambda_{det.}$ = 400 nm) and (c) emission spectrum (asterisk: second order of excitation light) and (d) excitation spectrum recorded at 77 K ($\lambda_{exc.}$ = 280 nm, $\lambda_{det.}$ = 400 nm); bottom: electronic spectra of **4b** (c = 8.5 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 ($\lambda_{exc.}$ = 300 nm, $\lambda_{det.}$ = 580 nm).

Due to their light sensitivity, the silver complexes were not investigated. The low-energy onset of the absorption of the gold(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 emission 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. 17200 cm^{-1}), we attribute this emission to an ^{3}IL excited state. The long emission decay time of the LE band of 0.73 ms at 77 K further supports this interpretation (Fig. S8 Supplementary Information). 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 (τ = 0.28 ms, see Figures S5 and S7 Supplementary Information).

In principle, the Au(III) complexes **5a,b** exhibit similar electronic spectra: Figure 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[AuBr$_4$], can be attributed to n(Br)$\rightarrow$5d$_{x2-y2}$ and π(Br)$\rightarrow$5d$_{x2-y2}$ 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 ^{3}IL excited state. The electronic spectra of **5a** are very similar (see Figure S6).

**Figure 6**. Electronic spectra of **5b** (c = 8.0 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).

Table 1. UV/Vis and emission spectroscopic data of compounds **2 – 5** in ethanol.

	Absorption λ_{max} [nm] (log $\square$ / l mol^{-1} cm^{-1})	Emission, λ_{max} [nm] 298 K[a]	77 K	Excitation, λ_{max} [nm] 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

As expected for NHC-Au(III) halides, complexes **5a**,**b** are light-sensitive and can be photoreduced to the Au(I) congeners.[7c,16] The photochemical reactivity of **5b** was investigated by irraditation of an ethanolic solution with polychromatic light (λ > 305 nm). As previously reported, NHC–Au(III) bromides undergo photo-reductive elimination of Br$_2$ and formation of the respective NHC–Au(I) bromide (no Br$_2$ could be detected because of the fast oxidation of the solvent).[7c] Figures 7 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(III) complex is completely photo-reduced. The absorption spectrum of the reduced species is superimposable with the spectrum of the Au(I) 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 gold(III) compound **5a**.
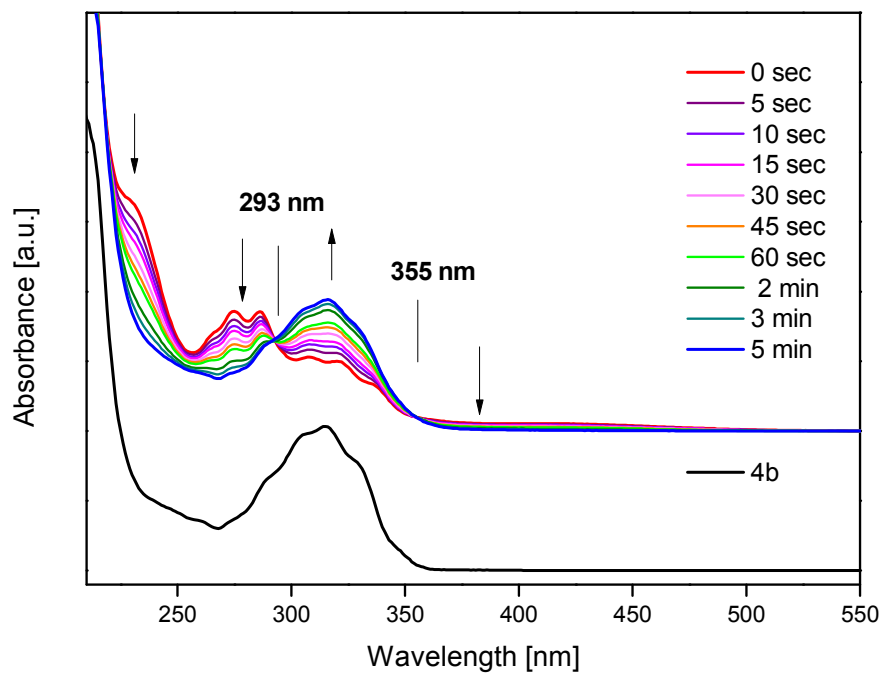
Figure 7: Irradiation of an ethanolic solution of **5b** (c = 9 10^{-5} M) with polychromatic light (λ > 305 nm). The lower, black graph shows the absorption of an ethanolic solution of **4b**.

Table 2: Crystal Data and Data Collection and Structure Refinement Details for Compounds **1a, 2a, 4a, 5a**.

Crystal Data	1a	2a	4a	5a
Empirical formula	$C_{14}H_{14}N_2$	$C_{15}H_{15}N_2PF_6$	$C_{15}H_{14}AuBrN_2$	$C_{15}H_{14}AuBr_3N_2$
Formula weight	210.27	368.26	499.16	658.98
Crystal size (mm)	0.41 x 0.37 x 0.32	0.42 x 0.26 x 0.05	0.57 x 0.17 x 0.18	0.63 x 0.24 x 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)
α (°)	90	90	90	90
β (°)	97.596 (4)	107.178 (15)	107.979 (7)	99.907 (7)
γ (°)	90	90	90	90
V (Å³)	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
μ (mm⁻¹)	0.07	0.24	12.95	15.57
T (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	21615	5480	8914	10864
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 Å⁻³)	0.21 / -0.19	0.25 / -0.24	3.84 / -1.87	1.02 / -0.96
Final R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0453$	$R_1 = 0.0518$	$R_1 = 0.0391$	$R_1 = 0.0412$
	$wR_2 = 0.1123$	$wR_2 = 0.1166$	$wR_2 = 0.1022$	$wR_2 = 0.0804$
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	5b*
Empirical formula	$C_{18}H_{22}N_2$	$C_{19}H_{23}N_2PF_6$	$C_{38}H_{44}N_4AgPF_6$	$C_{38}H_{44}N_4AuPF_6$	$C_{19}H_{22}AuBr_3N_2$
Formula weight	266.38	424.36	809.61	898.71	715.08
Crystal size (mm)	0.40 x 0.32 x 0.29	0.40 x 0.37 x 0.13	0.37 x 0.16 x 0.14	0.60 x 0.40 x 0.05	0.45 x 0.44 x 0.37
Crystal system	Tetragonal	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	$P\text{-}42_1c$	$Pna2_1$	$P\text{-}1$	$P\text{-}1$	$P2_1/n$
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)
c (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 (Å³)	3301.1 (4)	2027.4 (7)	928.1 (4)	941.95 (18)	2173.2 (14)
D_{calcd} (g cm⁻¹)	1.072	1.390	1.449	1.584	2.186
Z	8	4	1	1	4
μ (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	34152	27566	17396	75271	23730
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 R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0348$	$R_1 = 0.0553$	$R_1 = 0.0537$	$R_1 = 0.0375$	$R_1 = 0.0296$
	$wR_2 = 0.0851$	$wR_2 = 0.1498$	$wR_2 = 0.1100$	$wR_2 = 0.0933$	$wR_2 = 0.0619$
R 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

Conclusion

We have demonstrated that CsBr$_3$ can be used as an easy-to-handle 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(III) complexes are cleanly photo-reduced to the Au(I) congeners upon irradiation with polychromic light.

Acknowledgments

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 Institut für Technologie Organischer Stoffe at the Universität Linz. NMR spectra were recorded on a Bruker Avance III (300 MHz) spectrometer. ^{1}H and ^{13}C NMR shifts are reported in ppm relative to $Si(CH_3)_4$ and were referenced internally with respect to the residual signal of the deuterated solvent. Mass spectra were collected on a Finnigan LCQ DecaXPlus 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 and 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 contain the supplementary crystallographic data for compounds **1a-2a**, **4a-5a**, **1b-4b**, and **5b***. These data can be obtained free of charge from The Cambrige Crystallographic Data Centre at www.ccdc.cam.ac.uk.

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: 8.95 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.[26] ¹H-NMR (300 MHz, CDCl₃, δ [ppm]): 8.72 (d, 1H, $^3J_{HH}$ = 4.8 Hz), 8.37 (s, 1H, C*H*=N), 8.30 (d, 1H, $^3J_{HH}$ = 8 Hz), 7.83 (td, 1H $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.5 Hz), 7.42 (ddd, 1H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 1.2 Hz), 7.11 – 7.08 (m, 2H), 7.01 – 6.95 (m, 1H), 2.17 (s, 6H, C*H*₃). 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: 9.19 g (65.7%). The spectroscopic data correspond to the reported data.[27] ¹H-NMR (300 MHz, CDCl₃ δ [ppm]): 8.76 (d, 1H, $^3J_{HH}$ = 4.9 Hz), 8.38 (s, 1H), 8.32 (d, 1H, $^3J_{HH}$ = 7.8 Hz), 7.86 (t, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.42 (ddd, 1H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.2 Hz), 7.24 – 7.14 (m, 3H), 3.03 (sept, 2H, $^3J_{HH}$ = 6.9 Hz), 1.22 (d, 12H, $^3J_{HH}$

= 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, 0.0285 mol, 1 equ.), 4 M HCl in 1,4-dioxane (7.1 ml mol, 1 equ.) was added dropwise. After stirring for 15 h at ambient temperature, the solvent was seperated 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 KPF$_6$ was added to precipitate compound **2a** as a yellow solid. Yield: 2.753 g (43.6%). Slow gas-phase diffusion of diethyl ether into a diluted DCM solution gave colourless crystals suitable for X-ray diffraction. ^{1}H-NMR (300 MHz, DMSO, δ [ppm]): 9.96 (s, 1H), 8.60 (d, 1H, $^3J_{HH}$ = 7.0 Hz), 8.43 (s, 1H), 7.94 (d, 2H, $^3J_{HH}$ = 9.3 Hz), 7.54 - 7.48 (m, 1H), 7.41 – 7.36 (m, 3H), 7.32 – 7.27 (m, 1H), 2.06 (s, 6H). ^{13}C-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 C$_{15}$H$_{15}$N$_2$PF$_6$ (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** (9.194g, 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: 6.319 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. ^{1}H-NMR (300 MHz, DMSO, δ [ppm]): 10.01 (s, 1H), 8.61 (d, 1H, $^3J_{HH}$ = 7 Hz), 8.52 (s, 1H), 7.94 (d, 1H, $^3J_{HH}$ = 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). ^{13}C-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 [PF$_6$]$^-$. Anal. Calcd for C$_{19}$H$_{23}$N$_2$PF$_6$ (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-3-ylidene}silver(I) (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: 1.155 g (77.6%) of a yellow solid. ^{1}H-NMR (300 MHz, DMSO, δ [ppm]): 8.69 (d, 1H, $^3J_{HH}$ = 7 Hz), 7.93 (s, 1H), 7.65 (d, 1H, $^3J_{HH}$ = 9 Hz), 7.44 – 7.39 (m, 1H), 7.27 – 7.24 (m, 2H), 7.09 (dd, 1H $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 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 $C_{30}H_{28}N_4AgPF_6$ (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-3-ylidene}silver(I) (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: 2.215 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. ^{1}H-NMR (300 MHz, DMSO, δ [ppm]): 8.45 (d, 1H, $^3J_{HH}$ = 7 Hz), 8.06 (s, 1H,), 7.67 (d, 1H, $^3J_{HH}$ = 9 Hz), 7.53 – 7.48 (m, 1H), 7.29 – 7.27 (m, 2H), 7.12 (dd, 1H $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 9 Hz), 6.97 – 6.93 (m, 1H), 1.99 (sept, 2H, $^3J_{HH}$ = 7 Hz), 1.06 (d, 6H, $^3J_{HH}$ = 7 Hz), 0.82 (d, 6H, $^3J_{HH}$ = 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 $[C_{38}H_{44}N_4Ag]^+$, 417 $[C_{19}H_{22}N_2Ag + CH_3OH]^+$, 403 $[C_{19}H_{22}N_2Ag + H_2O]^+$, 385 $[C_{19}H_{22}N_2Ag]^+$. Anal. Calcd for $C_{38}H_{44}N_4AgPF_6$ (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-3-ylidene}gold(I) (4a)

Compound **3a** (0.501 g, 1.37 mmol) was dissolved in 10 ml dichloromethane. 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. ^{1}H-NMR (300 MHz, CDCl3, δ [ppm]): 8.62 (dd, 1H, $^3J_{HH}$ = 7 Hz), 7.44 (d, 1H,

$^3J_{HH}$ = 9 Hz), 7.36 – 7.31 (m, 1H), 7.21 – 7.17 (m, 3H), 7.00 (dd, 1H, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 9 Hz), 6.79 (td, 1H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 2.02 (s, 6 H). ^{13}C-NMR (75 MHz, CDCl$_3$, 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. ^{1}H-NMR (300 MHz, DMSO, δ [ppm]): 8.61 (d, 1H, $^3J_{HH}$ = 7 Hz), 8.01 (s, 1H), 7.69 (d, 1H, $^3J_{HH}$ = 9 Hz), 7.46 – 7.41 (m, 1H), 7.33 – 7.31 (m, 2H), 7.12 (dd, 1H, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 9 Hz), 6.97 (t, 1H, $^3J_{HH}$ = 7 Hz), 1.98 (s, 6H). ^{13}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$_4$Au]$^+$. Anal. Calcd for C$_{15}$H$_{14}$N$_2$AuBr (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(I) hexafluorophosphate (4b)

Compound **3b** (0.231 g, 0.55 mmol) was dissolved in 10 ml dichloromethane. 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 ^{1}H-NMR of the crude compound is not clean; it possibly shows a mixture of ionic and neutral gold(I) 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(I) 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. ^{1}H-NMR (300 MHz, CDCl$_3$, δ [ppm]): 8.11 (dd, 1H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 0.9 Hz), 7.56 – 7.48 (m, 2H), 7.29 – 7.23 (m, 3H), 7.09 (ddd, 1H, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 0.7 Hz), 6.94 (td, 1H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 2.07 (sept, 2 H, $^3J_{HH}$ = 7 Hz), 1.09 (d, 6H, $^3J_{HH}$ = 7 Hz), 0.97 (d, 6H, $^3J_{HH}$ = 7 Hz). ^{13}C-NMR (75 MHz, CDCl$_3$, 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 C$_{38}$H$_{44}$N$_4$AuPF$_6$ (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 [C$_{38}$H$_{44}$N$_4$Au]$^+$.

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 dichloromethane and cooled with ice bath. Solid CsBr$_3$ (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. ^{1}H-NMR (300 MHz, DMSO, δ [ppm]): 8.82 (d, 1H, $^3J_{HH}$ = 7 Hz), 8.45 (s, 1H), 7.84 (d, 1H, $^3J_{HH}$ = 9 Hz), 7.51 – 7.46 (m, 1H), 7.36 – 7.26 (m, 3H), 7.21 – 7.16 (m, 1H), 2.14 (s, 6H). ^{13}C-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 $[C_{30}H_{28}N_4AuBr]^+$, 641 $[C_{30}H_{28}N_4Au]^+$, 301 $[C_{15}H_{14}N_2Br]^+$. Anal. Calcd for $C_{15}H_{14}N_2AuBr_3$ (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(III) hexafluorophosphate (5b)

Compound **4b** (0.100 g, 0.11 mmol) was dissolved in 20 ml dichloromethane and cooled with ice bath. Solid $CsBr_3$ (0.070 g, 0.19 mmol, 1.7 equ.) 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 rust-brown powder. Yield: 0.112 g (95.5%). Slow gas-phase diffusion of diethyl ether into a dilute DCM solution gave bright red crystals. ^{1}H-NMR (300 MHz, DMSO, δ [ppm]): 9.00 (d, 1H, $^3J_{HH}$ = 7 Hz), 8.48 (s, 1H,), 7.82 (d, 1H, $^3J_{HH}$ = 9 Hz), 7.62 – 7.57 (m, 1H), 7.35 – 7.21 (m, 4H), 2.17 (sept, 2H, $^3J_{HH}$ = 7 Hz), 0.95 (d, 6H, $^3J_{HH}$ = 7 Hz), 0.87 (d, 6H, $^3J_{HH}$ = 7 Hz).^{13}C-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 $C_{38}H_{44}N_4AuBr_2PF_6$ (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-3-ylidene}gold(III) (5b*)

^{1}H-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, $^3J_{HH}$ = 7 Hz), 1.13 (d, 6H, $^3J_{HH}$ = 7 Hz), 1.06 (d, 6H, $^3J_{HH}$ = 7 Hz).

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Graphical Abstract
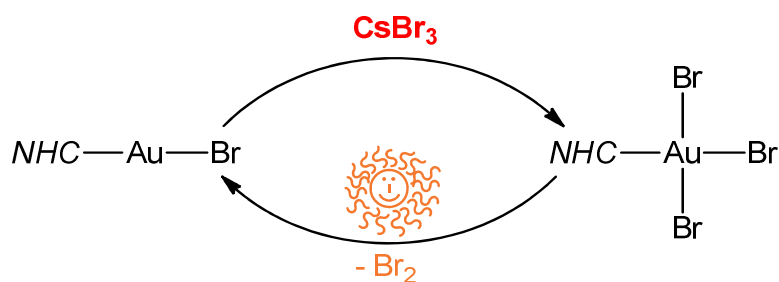
CsBr$_3$ was investigated as a new and convenient oxidant for NHC-Au(I) complexes for the preparation of the respective Au(III) complexes. The Au(I) complexes were synthesized by the silver salt method using [(NHC)$_2$Ag]PF$_6$ and (tht)AuBr. Oxidation with CsBr$_3$ gave the complexes (NHC)AuBr$_3$ and [(NHC)$_2$AuBr$_2$]PF$_6$ in high yields and purity, which proves the suitability of this reagent. The complexes were 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(III) complexes are cleanly photo-reduced to the Au(I) congener.