Pages: 10





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Synthesis, Characterization and Luminescence of Gold Complexes Bearing an NHC Ligand Based on the Imidazo[1,5-*a*]quinolinol Scaffold

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We report on the synthesis and characterization of an NHC ligand based on the imidazo[1,5-*a*]quinolinol scaffold. The benzyl-protected NHC precursor was used for the preparation of the corresponding Ag^{I} , Au^{I} and Au^{III} complexes. The molecular structures of the Au^{I} and Au^{III} halide complexes determined by single-crystal X-ray diffraction reveal con-

siderable distortion of the rigid NHC moiety due to steric repulsion between the gold and oxygen atoms. At ambient temperature, the complexes are weakly fluorescent from an intraligand excited state, whereas at 77 K the emission spectra are dominated by intraligand phosphorescence.

Introduction

N-Heterocyclic carbene (NHC) ligands with an extended π system have been the focus of intensive research in recent years due to their potential applications in catalysis and optoelectronics. Several metal complexes containing these NHCs as chromophores have been used as efficient triplet emitters in organic light-emitting devices (OLEDs) because they are highly stable and have favourable emission properties.^[1] Metal complexes containing 5d platinum group metals such as Ir^{III} and Pt^{II} have mostly been investigated.^[2] An interesting alternative to these metals might be gold in its I and III oxidation states.^[3] It is well known that Au^I complexes exhibiting aurophilic interactions give rise to emissive excited states.^[4-6] Those bearing ligands with huge π systems and energetically low-lying excited $\pi\pi^*$ states feature intense intraligand (IL) emissions.^[7-9] However, Au^{III} with its low-lying dd states causes effective quenching of the excited state, thus diminishing or even preventing luminescence.^[10] Therefore Au^{III} complexes are only emissive if strong ligands destabilize these dd states thereby hampering radiationless deactivation. Accordingly, these Au^{III} complexes contain, in addition to the chromophore, strong σ donating ligands such as alkynyl, isocyanide or

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Altenbergerstr. 69, 4040 Linz, Austria Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201300575. NHC.^[3,11–16] For this reason, combining a carbene function with an extended π system as the chromophoric unit should result in luminescent Au^{III} complexes. We have recently reported a 1,10-phenanthroline analogue NHC ligand (**A**) and the emissive properties of its Au^I and Au^{III} complexes.^[17] In this contribution we present a similar NHC with an ether oxygen atom as the second binding site that forms a potential chelating ligand (**B**) similar to 10-hydroxybenzo[*h*]quinoline (**C**, Scheme 1).



Scheme 1. NHCs A and B, and 10-hydroxybenzo[h]quinolone (C).

Results and Discussion

Synthesis and Characterization

The NHC precursor **3** was synthesized starting from the previously reported benzyl-protected 8-benzyloxyquinoline-2-carbaldehyde (**1**), which was obtained from commercially available 2-methyl-8-hydroxyquinoline by treatment with sodium metal and benzyl chloride in 2-propanol and subsequent oxidation of the resulting 2-methyl-8-(benzyloxy)-quinoline with SeO₂.^[18] Upon work-up, yellow crystals of 8-(benzyloxy)quinoline-2-carbaldehyde were formed. Condensation of the aldehyde with the primary amine 2,6-diiso-propylaniline gave the Schiff base **2** (Scheme 2). Cyclization

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with paraformaldehyde and dry HCl yielded the carbene precursor **3** as an off-white powder in good yield and purity.^[19] Note that a considerable amount of a side-product was formed if the formaldehyde was not completely dissolved in toluene at the beginning of the reaction. Partial hydrolysis of **2** proceeded easily under the acidic conditions of the reaction and led to the regeneration of compound **1**, which can function as the carbonyl component instead of formaldehyde. A homogeneous reaction mixture favoured the formation of compound **3**, thus preventing its contamination.



Scheme 2. Synthesis of NHC precursor **3** and its Ag and Au complexes **4**–**6**.

Reaction of the imidazolium chloride 3 with an excess of Ag₂O under ambient conditions yielded the Ag^I-carbene complex 4. As no crystals of this compound could be grown, its constitution is not completely certain. It is known that NHC-silver halides undergo ligand-scrambling reactions to form either neutral or ionic complexes of the form NHC-Ag-X and [(NHC)₂Ag][AgX₂], respectively. However, the ¹³C NMR shifts of the carbon atoms of the two forms are too similar to allow the isomers to be distinguished.^[20] A thorough investigation of 4 was further hampered by the instability of the compound in solution: no ¹³C NMR spectrum could be recorded because of decomposition during the measurement. Therefore we compared the molar conductivity of 4 with the molar conductivity of a previously reported ionic complex [(NHC)₂Ag]-[AgX₂] in dichloromethane (dcm).^[21] Because of the similar $1.4 \ \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1};$ reference values **[4**: sample: 1.1 Ω^{-1} cm²mol⁻¹ (see the Exp. Sect.)] we can infer that 4 has an ionic form. Transmetallation of **4** with [(dms)AuCl] (dms = dimethyl sulfide) yielded the NHC–Au^I complex **5** as a yellow solid, which was oxidized with Br₂ at -50 °C to the corresponding red NHC–Au^{III} complex **6**.

All compounds exhibit the expected ¹H NMR spectra (see the Exp. Sect.). In the ¹H NMR spectra, the resonance of the imidazolium proton at $\delta = 10.83$ ppm (in [D₆]dmso) vanishes upon complex formation. ¹³C NMR resonances of the carbene carbon atoms appear at 175.6 (NHC–Au^I complex **5**) and 148.1 ppm (NHC–Au^{III} complex **6**), which are very similar to the analogous complexes bearing ligand **A**.^[17] The corresponding carbon atom of the imidazolium chloride **3** resonates at $\delta = 148.7$ ppm.

Due to ligand-exchange reactions, the mass spectra of the NHC-M complexes (M = Ag, Au) are usually dominated by the ionic species $[(NHC)_2M]^+$ irrespective of the actual composition in the solid state.^[22,23] Interestingly, in the ESI mass spectrum of NHC-Au^I complex 5, not only the signal of [(NHC)Au]⁺ but also of the chloronium species $[{(NHC)Au}_2Cl]^+$ can be detected. The chloronium cation can be formed by facile halide elimination with the formation of $[(NHC)Au]^+$ and its subsequent reaction with 5. The formation of chloronium and bromonium species $[{(NHC)Au}_2Cl]^+$ and $[{(NHC)Au}_2Br]^+$ can also be observed for 6. This is a result of the easy reductive elimination of halogens from Au^{III}-halides to yield (NHC)AuCl/ Br. The mass spectroscopic detection of halonium ions $[(LAu)_2X]^+$ (X = Cl, Br) is common for phosphane gold(I) complexes, but relatively seldom reported for L = NHC.^[24] Note that the corresponding complexes $[(LAu)_2X]Y$ (L = R_3P , Y = weakly coordinating anion) have previously been prepared and structurally characterized.^[25]

Structural Studies

Compounds 1–3, 5 and 6 were characterized by singlecrystal X-ray diffraction. Yellow needles of 8-benzyloxyquinoline-2-carbaldehyde (1) were obtained upon work-up. The compound crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Figure 1, top). All geometric parameters are in the range expected.^[26] The aldehyde group is coplanar with the aromatic ring plane and the oxygen atom is in a *trans* position relative to the nitrogen atom of the quinoline moiety. Yellow needles of **2** were obtained upon recrystallization in ethanol. The compound crystallizes in the orthorhombic space group *Pbca* with one molecule of the *E* isomer in the asymmetric unit showing the expected structural features (Figure 1, bottom).

Compound 3 crystallizes in the monoclinic space group $P2_1/c$. The bond lengths and angles are as expected. Despite their common charges and bulky substituents, the cations aggregate to form dimers through π - π stacking interactions with relatively short distances between the planes of about 3.4 Å (Figure 2, bottom). As previously mentioned, the Ag^I-carbene is not stable in solution. During slow gasphase diffusion of diethyl ether into a dilute chloroform

Pages: 10

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Figure 1. Molecular structures of 1 (top) and 2 (bottom; ellipsoids drawn at the 50% probability level, H atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°] for 1: C1–O1 1.206(2), C2–N1 1.324(2), C3–N1 1.366(2), C4–O2 1.364(2), O1–C1–C2 123.4(2); for 2: N2–C1 1.267(1), C2–N1 1.324(1), C3–N1 1.365(1), C4–O1 1.362(1), N2–C1–C2 121.0(1).

solution of 4, the complex decomposes. As a result, very few colourless crystals of the imidazolium salt with $[AgCl_2]^-$ as the counter ion suitable for X-ray diffraction were obtained. The imidazolium dichloroargentate crystallizes in the monoclinic space group $P2_1/n$ (Figure 3). No aggregation of the anions through argentophilic interactions was observed. The parameters of the cation are very similar to those of the chloride salt 3.

The molecular structure of **5** is depicted in Figure 4. Interestingly, the aromatic moiety deviates considerably from planarity (Figure 4, bottom). This deformation is clearly a result of the steric repulsion between the oxygen and gold atoms. Due to the geometrical constraint of the ligand, there is an Au···O contact of 2.84(1) Å, which is well below the sum of the van der Waals radii $[r(Au) + r(O) = 3.18 \text{ Å}].^{[27]}$ However, its classification as a T-coordinated complex, although not unknown in Au^I complexes,^[28] is not justified in this case. We therefore infer that the Au^I atom is linearly coordinated to the carbene carbon atom and the chloride [C1–Au1–Cl1 177.0(1)°] with Au1–C1 and Au1–





Figure 3. Molecular structure of the imidazolium cation of imidazolium dichlororargentate **3**·AgCl. Selected bond lengths [Å] and angles [°]: C1–N1 1.33(1), C1–N2 1.35(1), N2–C1–N1 108.2(5), Ag1–Cl1 2.308(2), Ag1–Cl2 2.318(2), Cl2–Ag1–Cl1 170.8(1).



Cl1 distances of 1.99(1) and 2.285(2) Å, respectively, which is within the range of reported values. The shortest Au–Au distance is around 8.8 Å, longer than the aurophilicity limit of approximately 3.5 Å. Thus, no π - π interactions of the extended π system of the NHC moiety analogous to **3** are present in the crystals.



Figure 4. Molecular structure of **5**. Illustration of the strong deformation of the aromatic moiety (bottom). Selected bond lengths [Å] and angles [°]: Au1–C1 1.99(1), Au1–Cl1 2.285(2), C1–N2 1.37(1), C1–N1 1.34(1), C1–Au1–Cl1 177.0(1), N1–C1–N2 104.8(6), N1–C1–Au1 123.1(5), N2–C1–Au1 130.9(6), C1–Au1–O1 70.8(5), Au1–O1 2.84(1).

Au^{III} complex **6** crystallizes in the monoclinic space group $P2_1/n$ and contains one complex and one chloroform molecule in the asymmetric unit. The gold atom is surrounded by the carbon carbon atom C1, the three halogen



Figure 5. Molecular structure of **6** (top) and the distorted coordination environment around the gold atom (bottom). The chloroform molecule has been omitted for clarity. Selected bond lengths [Å] and angles [°]: Au1–C1 2.010(6), Au1–Cl1 2.331(2), Au1–Br1 2.427(1), Au1–Br2 2.417(1), C1–N1 1.39(1), C1–N2 1.34(1). C1–Au1–Cl1 175.7(2), C1–Au1–Br2 92.5(2), Cl1–Au1–Br2 90.40(4), Br2–Au1–Br1 177.63(3), C1–N1–C2 111.8(5), N1–C1–Au1 122.3(5), N2–C1–Au1 129.8(5), O1–Au1–Cl 73.92(4).

atoms in square-planar positions and the oxygen atom of the ether group in an axial position (Figure 5). As observed for other mixed (NHC)AuXY₂ (X, Y = halide) complexes, the more electronegative chloride is in a *trans* position relative to the carbene carbon atom.^[21,23] All Au–C and Au–

Table 1. UV/Vis and emission spectroscopic data of solutions of compounds 3, 5, and 6.

	Absorption: λ_{\max} [nm] [log(ε /lmol ⁻¹ cm ⁻¹)]	Excitation: λ _{max} [nn 298 K	n] 77 K	Emission: λ _{max} [nm 298 K] 77 K	Quantum yield [%]
3	233 [4.22], 262 [4.33], 270 [4.37], 280 [4.15], 291 [3.98], 303 [4.04], 318 [3.96], 331 [3.48] ^[a]	332, 317, 303, 289, 272 ^[a]	329, 320, 315, 305, 292, 279, 268, 264 ^[b]	337, 351, 368, 390 (sh) ^[a,c]	330, 346, 368, 385 ^[b]	19 ^[a]
5	270 [4.00], 282 [4.13], 292 [4.24], 321 [3.97] ^[a]	331, 317, 303, 289, 268 ^[b]	348, 330, 318, 294, 292, 282 ^[b]	353, 369, 393 (sh), 490 ^[a]	346, 363, 384, 521, 568, 621, 691 ^[b]	0.2 ^[a]
6	330 [3.99], 316 [4.08], 304 [4.02], 285 [4.17], 275 [4.24] ^[a]	334, 318, 303, 293, 290, 281, 268, 262 ^[a]	348, 330, 316, 304, 293, 282 ^[b]	354, 369 ^[b]	346, 363, 420, 522, 568, 621, 690 ^[b]	0.05 ^[a]

[a] Dichloromethane. [b] Ethanol. [c] sh: shoulder.

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halide distances are in the expected range. Compared with 5, the Au-O distance decreases significantly to 2.717(1) Å, presumably due to the higher charge of the coordinated metal. Again, the orientation of the ligand towards the metal indicates the low oxophilicity of gold: the aromatic moiety is less twisted than in 5, but the angle between the NHC moiety plane and the vector Au1-C1 is only around 160°. Unlike in non-distorted systems, the Au1–C1 bond does not lie on the line bisecting the N1-C1-N2 angle in the case of compound 6. It is clear that the geometry and rigidity of the ligand imposes a square-pyramidal coordination environment, and the gold and oxygen atoms try to avoid close contact. This is in contrast to a related aminefunctionalized NHC ligand in which a square-pyramidal coordination was observed although the pendant amine was not forced due to the rigidity of the ligand framework.^[21] Other examples of a square-pyramidal coordination environment are documented for diimine-type ligands such as phen and 2,2'-bipyridine in $[(N \cap N)AuCl_3]$ complexes.^[29] This coordination geometry was also found for the corresponding Au^{III} complex bearing ligand A.^[17]

Electronic Spectra

The absorption spectrum of the imidazolium salt 3 shows a structured band with maxima at 270, 291, 303, 318 and 331 nm, and two shoulders at 262 and 280 nm (Table 1). Due to their high extinction coefficients, the signals can be assigned to π - π * transitions, possibly masking additional $n-\pi^*$ transitions. The emission spectrum at room temperature shows a well-resolved vibronic structure with three main peaks at 337, 351 and 368 nm with a shoulder at 390 nm. A small Stokes shift of 540 cm⁻¹ and an energy $E_{(0-0)}$ of 30000 cm⁻¹ can be derived for the first excited state. The emission quantum yield is 19%. As expected, the vibronic structure is much better resolved and slightly narrowed in the low-temperature luminescence spectra recorded at 77 K, but no additional emission band evolves (Figure 6). This behaviour is typical of aromatic chromophores with an extended π system.

Because of its light sensitivity, no photophysical measurements were performed on complex 4. The absorption spectrum of the NHC-Au^I complex 5 shows a structured band with maxima at 282, 292 and 321 nm with a shoulder at 270 nm (Figure 7 and Table 1). As with 3, these bands can be assigned to $\pi - \pi^*$ transitions that are in good agreement with their high extinction coefficients; possible $n-\pi^*$ transitions might be masked. The emission spectrum at room temperature displays a structured high-energy (HE) band comparable to that of the imidazolium salt at 353, 369 and 393 (sh) nm, and a broad lower-energy (LE) emission band at around 490 nm. Because the HE bands of 3 and 5 nearly coincide, this emission can be assigned to IL fluorescence. Interestingly, the ratio of the intensities of the low- and high-energy bands decreases with decreasing concentration (Figure 8), which indicates an excimer character of the LE band. The nature of the excimer is not completely



Figure 6. Electronic spectra of 3: (a) absorption, (b) emission and (c) excitation spectra recorded at 298 K ($c = 5.0 \times 10^{-5}$ M in dcm, $\lambda_{\rm exc.} = 300$ nm, $\lambda_{\rm det.} = 390$ nm) and (d) emission spectrum recorded at 77 K and (e) excitation spectrum recorded at 77 K ($c = 2.5 \times 10^{-6}$ M in ethanol, $\lambda_{\rm exc.} = 300$ nm, $\lambda_{\rm det.} = 380$ nm).

clear: neither π - π stacking nor aurophilic interactions were observed in the solid-state structure, although these may exist transiently in solution. The solid-state structure of the imidazolium salt **3** shows that close contact of the π systems of two NHC ligands is possible despite the bulky substituents, whereas contact between the well-shielded gold atoms appears unlikely. In the emission spectrum of a thoroughly degassed solution of **5**, no further luminescence peaks evolved.

At 77 K in ethanol glass, the luminescence spectrum of **5** is dominated by structured long-wavelength emissions at 521, 568 and 621 nm. The average spacing between the peaks is around 1545 cm⁻¹, which roughly concurs with the tabulated ring-stretching frequencies of the aromatic molecules. At higher energy, less intense emission bands from IL fluorescence and a broad peak (presumably of excimer nature) are observed. Considering the huge Stokes shift (ca. 9540 cm⁻¹) and the structure of the LE band, we assign this emission to an ³IL excited state. The very long emission decay time of the LE band of 1.90 ms at 77 K also supports this interpretation. A similar emission spectrum was obtained for a sample of neat **5** at 298 K (see Figure S1 in the Supporting Information), which indicates the efficient quenching of the triplet state in liquid solution.

At 77 K, dual emission or dominance of the phosphorescence is not unusual for gold complexes bearing chromophores with an extended π system, and has frequently been reported in recent years.^[7,17,30,31] Despite the high atomic number of gold, the spin–orbit coupling promoted by the gold atom is comparably low and leads to relatively long phosphorescence lifetimes at 77 K, but it is high enough to allow for efficient S₁–T₁ intersystem crossing. This behaviour can be traced back to the low-lying d orbitals, which are not involved in low-energy electronic transitions. As the metal d orbitals do not directly participate in these transitions, the spin–orbit coupling is moderate and comparable /KAP1

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Figure 7. Top: electronic spectra of **5** in ethanol: (a) absorption, (b) emission and (c) excitation spectra recorded at 298 K ($c = 8 \times 10^{-5}$ M, $\lambda_{exc.} = 300$ nm, $\lambda_{det.} = 370$ nm) and (d) emission and (e) excitation spectra recorded at 77 K ($c = 2 \ 10^{-4}$ M, $\lambda_{exc.} = 300$ nm, $\lambda_{det.} = 570$ nm). Bottom: electronic spectra of **6** in ethanol: (a) absorption, (b) emission and (c) excitation spectra recorded at 298 K ($c = 5 \times 10^{-5}$ M, $\lambda_{exc.} = 300$ nm, $\lambda_{det.} = 370$ nm) and (d) emission and (e) excitation spectra recorded at 77 K ($c = 5 \times 10^{-5}$ M, $\lambda_{exc.} = 300$ nm, $\lambda_{det.} = 520$ nm).

to the "external heavy atom effect" observed for solvents containing heavy elements.^[7] It should be mentioned that Gray and co-workers postulated a non-emissive excimer state to explain the concentration-dependent phosphores-cence intensities of some aryl–gold(I) complexes.^[31–33] For **5**, IL fluorescence, excimer emission and IL phosphorescence can be observed at 77 K.

NHC–Au^{III} bromide complexes usually feature a weak LMCT band at around 335 nm. However, this band is obscured by the more intense π – π * transitions of the annulated NHC moiety in complex **6**. The (pseudo-)square-py-ramidal coordination environment of **6** destabilizes the d_{z²} orbital leading to a dd excited state as the lowest-energy transition,^[21] as indicated by a long absorption tail above 350 nm. At 298 K, only a weak emission band with two



Figure 8. Concentration-dependent emission of **5** in ethanol at 298 K (not degassed, $\lambda_{exc.} = 300$ nm, normalized to the same intensity at 353 nm).



Figure 9. Irradiation of a methanolic solution of **6** ($c = 4.1 \times 10^{-5}$ M) with polychromatic light ($\lambda > 305$ nm). Dotted curve shows the absorption of a methanolic solution of **5**.

maxima at 354 and 369 nm can be detected. Again, at 77 K the spectrum is dominated by an LE emission with three well-defined maxima at 522, 568 and 621 nm (spacing ca. 1570 cm⁻¹), which is comparable to the LE emission of **5** and can be assigned to IL phosphorescence. The emission decay time of the LE band is 1.51 ms at 77 K and supports this assignment. As expected for an Au^{III} halide, complex 6 is sensitive to light and is photoreduced to the Au^I congener. As a further deactivation path of the excited state exists, the photoreactivity is also accompanied by a significant decrease in the emission quantum yield to 0.05%.[34] The photochemical reactivity of 6 was tested by irradiation of a methanolic solution with polychromatic light ($\lambda > 305$ nm). As reported recently, NHC-Au^{III} bromides undergo photoreductive elimination of Br2 to form the corresponding NHC-Au^I bromide.^[17,23] Figure 9 illustrates the spectral changes of complex 6 upon irradiation for 10 min. Initially, the spectrum shows LE bands at 330, 315, 304, 285 and

Pages: 10

274 nm, HE absorption bands at 325 and 228 nm, and a long dd absorption tail above 340 nm. The photoreductive elimination of bromine occurs during the first seconds of irradiation, and after 10 min the Au^{III} complex is completely photoreduced. The absorption spectrum of the reduced species features bands at 321, 391 and 281 nm, and a shoulder at 325 nm. The absorption bands can be super-imposed on those of the Au^I complex **5**. Likewise, the long absorption tail vanishes upon irradiation, which is in accordance with the colour change of the solution from yellow to colourless. Four isosbestic points, at 288, 297, 336 and 350 nm, are indicative of clean photoreduction.^[35]

Conclusions

We have presented the synthesis and characterization of an annulated NHC ligand that is based on the imidazo[1,5*a*]quinolinol scaffold. The benzyl-protected NHC precursor was used to prepare the corresponding Ag^I, Au^I and Au^{III} complexes. The molecular structures of the Au^{I} and $\mathrm{Au}^{\mathrm{III}}$ complexes determined by single-crystal X-ray diffraction reveal a considerable distortion of the rigid NHC moiety due to steric repulsion of the gold and oxygen atoms. The emission properties of the gold complexes depend significantly on temperature: at ambient temperature the complexes are weakly emissive from an ¹IL excited state, whereas at 77 K the emission spectra are dominated by IL phosphorescence. For the NHC-Au^I complex, we observed concentration-dependent emission spectra, indicative of excimer formation in solution. Preparative work to deprotect the phenolic oxygen and synthesize a potential mono-anionic carbene ligand is underway.

Experimental Section

General: All reactions and manipulations of air- and/or moisturesensitive compounds were carried out in 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. [(dms)AuCl] (dms = Me₂S) was synthesized from gold, HCl, and dmso following a published procedure.^[36] 8-Benzyloxyquinoline-2-carbaldehyde (1) was prepared from 2-methyl-8benzyloxyquinoline by oxidation with SeO₂ following a published procedure.^[18]

Elemental analyses were carried out by the Institute for Chemical Technology of Organic Materials, Johannes Kepler University Linz. NMR spectra were recorded with a Bruker Digital Avance DPX 200 (200 MHz), Avance III (300 MHz) or Avance DRX 500 (500 MHz) spectrometer. ¹H and ¹³C NMR shifts are reported in ppm relative to Si(CH₃)₄ and are referenced internally to the residual signal of the deuteriated solvent. Mass spectra were recorded with a Finnigan LCQ DecaXPlus ion-trap mass spectrometer with an ESI ion source.

Spectroscopic-grade solvents were used for all photophysical characterizations. Absorption spectra were recorded with a Varian Cary 300 double-beam spectrometer. Emission spectra at 300 and 77 K were recorded with a Jobin–Yvon Fluorolog 3 steady-state fluorescence spectrometer. Before recording the emission and excitation spectra, the samples were degassed by at least three freeze–pump– thaw cycles. The photoluminescence quantum yields were determined relative to quinine sulfate as standard. Luminescence lifetimes were measured by using a Fluorolog FL-1040 phosphorimeter accessory. The estimated experimental errors are 5% in the molar absorption coefficients and fluorescence lifetimes, and 15% in the fluorescence quantum yields.^[37] The irradiation experiments were performed with an HBO 100 W lamp using polychromatic light with $\lambda > 305$ nm (WG305 filter). Conductivities were measured with a four-electrode conductivity cell, model TetraCon 96 (WTW). The reference sample [(NHC)₂Ag][AgCl₂] {NHC = 1-[2-(diisopropylamino)ethyl]-3-methylimidazol-2-ylidene} was synthesized in a previous study and the structure was verified by singlecrystal X-ray diffraction.^[21] Concentrations of the reference and complex **4** were identical.

Single-crystal structure analysis of compounds 1, 3, 3·AgCl, 5 and 6 was carried out with a Bruker Smart X2S diffractometer and single-crystal structure analysis of compound 2 was performed with a Bruker D8 Quest diffractometer using Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Further crystallographic and refinement data can be found in Table 2. The structures were solved by direct methods (SHELXS-97)^[38] and refined by full-matrix least-squares on F^2 (SHELXL-97).^[39] The H atoms were calculated geometrically and a riding model was applied during the refinement process. The chloride anion of the imidazolium chloride **3** was found to be disordered and no unequivocal atomic position could be determined. Therefore this disordered atom was treated as a diffuse contribution by using the SQUEEZE routine in the PLATON software package.^[40] The sqf file produced by PLATON, which contains the SQUEEZE results, is appended to the cif file.

CCDC-921406 (for 1), -921407 (for 2), -921408 (for 3), -921409 (for 3·AgCl), -921410 (for 5) and 932544 (for 6) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

N-(2',6'-Diisopropylphenyl)-8-(benzyloxy)quinolin-2-ylmethylenimine (2): 8-(Benzyloxy)quinoline-2-carbaldehyde (1; 1.60 g, 6.1 mmol) was dissolved in ethanol (5 mL) upon heating and 2,6diisopropylaniline (purity 92%, 2 mL, 9.7 mmol) was added. Subsequently a yellow precipitate formed, which was purified by recrystallization in ethanol, yield 2.17 g (83%). ¹H NMR (300 MHz, CDCl₃): δ = 8.52 (s, 1 H, HC=N), 8.39 (d, ³J_{HH} = 8.6 Hz, 1 H), 8.16 (d, ${}^{3}J_{\rm HH}$ = 8.6 Hz, 1 H), 7.48–7.45 (m, 2 H), 7.37 (d, $J_{\rm HH}$ = 4.8 Hz, 2 H), 7.29–7.21 (m, 2 H), 7.16–7.02 (m, 2 H), 5.28 (s, 2 H, O-CH₂), 2.95 [sept, $J_{\rm HH}$ = 6.8 Hz, 2 H, CH- $(CH_3)_2$], 1.10 [d, J_{HH} = 6.8 Hz, 12 H, $CH(CH_3)_2$] ppm. ¹³C NMR $(75 \text{ MHz}, \text{ CDCl}_3, 30 \text{ °C})$: $\delta = 163.8, 154.8, 153.6, 148.5, 140.3,$ 137.1, 136.9, 136.7, 130.4, 128.6, 128.0, 127.8, 127.0, 124.4, 123.0, 120.1, 118.7, 111.0, 71.1, 28.0, 23.4 ppm. MS (ESI pos): m/z = 445 $[C_{29}H_{30}N_2ONa]^+$, 423 $[C_{29}H_{31}N_2O]^+$. $C_{29}H_{30}N_2O$ (422.57): calcd. C 82.43, H 7.16, N 6.63; found C 82.07, H 7.13, N 6.65.

Limidazolium Chloride Derivative 3: The reaction was carried out in dry nitrogen. Paraformaldehyde (0.35 g, 11.2 mmol) was completely dissolved in hot toluene (30 mL) and N-(2',6'-diisopropylphenyl)-8-benzyloxyquinolin-2-ylmethylenimine (4.72 g, 11.2 mmol) was added. A 4 M HCl solution in 1,4-dioxane (2.8 mL, 11.2 mmol) was added dropwise and a red precipitate formed immediately. After stirring for 15 h at ambient temperature, the precipitate was filtered and washed with diethyl ether (5 mL). To remove unreacted paraformaldehyde, the residue was dissolved in dichloromethane and filtered. The solvent was removed under reduced pressure, and a pale-yellow residue was obtained.



Table 2.	Crystal da	ata and	data	collection ar	id structure	refinement	details for	or compoun	ds 1,	2, 3	, 3∙Ag	Cl, 5	s and	6
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	1	2	3	3·AgCl	5	6
Formula M _w	C ₁₇ H ₁₃ NO ₂ 263.28	C ₂₉ H ₃₀ N ₂ O 422.55	C ₃₀ H ₃₁ N ₂ O 435.57	C ₃₀ H ₃₁ AgCl ₂ N ₂ O 614.34	C ₃₀ H ₃₀ AuClN ₂ O 666.98	C ₃₁ H ₃₁ AuBr ₂ Cl ₄ N ₂ O 946.16
Crystal size	$0.37 \times 0.43 \times 0.71$	$0.118 \times 0.263 \times 1.759$	$0.13 \times 0.40 \times 0.63$	$0.05 \times 0.18 \times 0.50$	$0.13 \times 0.31 \times 0.53$	$0.05 \times 0.07 \times 0.51$
[IIIII] Cmutal autom		anth anh anala'a				
Crystal system	monoclinic	orthornombic	monocimic	monoclinic	monochnic	monoclinic
Space group	$P2_1/c$	Pbca	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
	8.1562(8)	16.667(1)	12.4346(10)	14.6/2(2)	10.4332(11)	10.1530(9)
<i>b</i> [A]	18.3255(18)	12.114(1)	12.4728(9)	11.7643(15)	18.705(2)	23.547(3)
<i>c</i> [A]	9.1463(8)	23.607(1)	17.1958(15)	16.271(2)	13.7404(14)	13.9529(13)
a [°]	90	90	90	90	90	90
β [°]	102.173(3)	90	96.396(3)	101.422(4)	94.888(4)	90.492(3)
γ [°]	90	90	90	90	90	90
V [Å ³]	1336.3(2)	4766.3(3)	2650.4(4)	2752.8(7)	2671.7(5)	3335.6(6)
$\rho_{\rm calcd}$ [g cm ⁻¹]	1.309	1.178	1.092	1.482	1.658	1.884
Z	4	8	4	4	4	4
μ [mm ⁻¹]	0.09	0.07	0.07	0.95	5.63	7.15
	200	100	201	200	200	200
θ range [°]	3 2-25 0	2,1-25,0	1 7-24 7	1.7-20.1	3 0-25 0	2 2-25 3
Reflections col-	8478	101156	16287	32604	17049	64151
lected	0170	101100	1020,	02001	1,019	01101
Unique reflec-	2339	4189	4488	2579	4704	5955
tions	2337	4107		2319	+/0+	5755
Observed reflec-	1785	3710	2996	1962	3456	4382
tions $[I > 2\sigma(I)]$						
Parameters re-	181/0	294/0	303/0	329/0	320/0	374/0
fined/restrained						
Absorption cor-	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
rection						
Tmin. Tmax	0.94, 0.97	0.7160. 0.7459	0.96. 0.99	0.65/0.95	0.15, 0.53	0.12, 0.72
σ_{a} (max/min)	0.19/_0.16	0 24/_0 19	0.31/_0.15	0.73/-0.32	1 09/_0 99	0.82/_0.84
$[e Å^{-3}]$	0.197 0.10	0.2.7 0.17	0.01/ 0.10	0		0.01
$R_1 [I \ge 2\sigma(I)]$	0.040	0.032	0.061	0.037	0.041	0.036
WR_{a}	0.108	0.084	0.166	0.095	0.103	0.084
w1v2	0.100	0.007	0.100	0.075	0.105	0.007

Recrystallization in ethanol gave **3** as a white solid, yield 0.33 g (61%). Slow gas-phase diffusion of diethyl ether into a diluted dcm solution gave colourless needles suitable for X-ray diffraction. ¹H NMR (300 MHz, [D₆]dmso, 30 °C): δ = 10.83 (s, 1 H, N-CH-N), 8.61 (s, 1 H), 7.79–7.50 (m, 10 H), 7.33–7.23 (m, 3 H), 5.66 (s, 2 H, O-CH₂), 2.33 [sept, *J*_{HH} = 6.8 Hz, 2 H, C*H*(CH₃)₂], 1.19–1.15 [m, 12 H, CH(CH₃)₂] ppm. ¹³C NMR (75 MHz, [D₆]dmso, 30 °C): δ = 148.7, 145.1, 136.0, 132.6, 131.5, 131.2, 129.7, 128.8, 128.4, 128.1, 127.8, 127.1, 126.9, 124.3, 121.0, 120.0, 116.9, 115.9, 114.0, 69.7, 27.9, 23.9 ppm. HRMS (ESI): calcd. for C₃₀H₃₁N₂O 435.2431 [C₃₀H₃₁N₂O]⁺; found 435.2424.

Silver(I) Complex 4: In a flask covered with aluminium foil, 3 (0.210 g, 0.45 mmol) was dissolved in dcm (5 mL). Ag₂O (0.110 g, 0.47 mmol) was added whilst stirring, and a precipitate of AgCl formed immediately. After stirring for 3 h at ambient temperature, the reaction mixture was filtered. The solvent was removed in vacuo, the residue was dissolved in a small amount of dcm, and diethyl ether was added to precipitate 4 as a light-brown solid, yield 0.190 g (74%). ¹H NMR (300 MHz, [D₆]dmso, 30 °C): δ = 8.28 (s, 1 H), 7.65-7.42 (m, 11 H), 7.31-7.29 (m, 3 H), 5.64 (s, 2 H, O- CH_2), 2.27 [sept, J_{HH} = 6.7 Hz, 2 H, $CH(CH_3)_2$], 1.21 [d, J_{HH} = 6.7 Hz, 6 H, CH(CH₃)₂], 1.16 [d, J_{HH} = 6.7 Hz, 6 H, CH- $(CH_3)_2$ ppm. ¹³C NMR (75 MHz, [D₆]dmso, 30 °C): decomposition during measurement. MS (ESI pos): m/z = 977 $[C_{60}H_{60}N_4O_2Ag]^+, \quad 543 \quad [C_{30}H_{30}N_2OAg]^+, \quad 435 \quad [C_{30}H_{31}N_2O]^+.$ C₃₀H₃₀AgClN₂O (577.90): calcd. C 62.35, H 5.23, N 4.85; found C 62.63, H 5.24, N 4.85.

Gold(I) Complex 5: Compound 4 (70 mg, 0.12 mmol) was dissolved in dcm (5 mL). Solid [(dms)AuCl] (35 mg, 0.12 mmol) was added to the stirred solution, and a precipitate of AgCl formed immediately. After stirring for 60 min at ambient temperature, the AgCl was filtered off. The product was precipitated with diethyl ether as a yellow solid. Slow gas-phase diffusion of pentane into a diluted dcm solution gave yellow crystals of 5 suitable for X-ray diffraction, yield 40 mg (50%). ¹H NMR (300 MHz, CDCl₃, 30 °C): δ = 7.46– 7.29 (m, 4 H), 7.22-7.07 (m, 10 H), 5.38 (s, 2 H, O-CH₂), 2.23 [sept, $J_{\rm HH}$ = 6.8 Hz, 2 H, CH(CH₃)₂], 1.12 [d, $J_{\rm HH}$ = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.02 [d, J_{HH} = 6.8 Hz, 6 H, $CH(CH_3)_2$] ppm. ¹³C NMR (75 MHz, CDCl₃, 30 °C): δ = 175.6, 150.5, 145.6, 135.9, 135.5, 131.1, 130.6, 128.6, 128.4, 128.3, 128.0, 127.4, 126.0, 124.1, 123.1, 120.4, 115.4, 114.2, 114.0, 70.4, 28.5, 24.4, 24.0 ppm. ¹H NMR (500 MHz, [D₆]dmso, 30 °C): δ = 8.21 (s, 1 H), 7.54–7.25 (m, 13 H), 5.37 (s, 2 H, O-C H_2), 2.16 [sept, J_{HH} = 6.8 Hz, 2 H, CH(CH₃)₂], 1.09–1.06 [m, 12 H, CH(CH₃)₂] ppm. MS (ESI pos): $m/z = 1297 [C_{60}H_{60}N_4O_2Au_2Cl]^+, 668 [C_{30}H_{31}N_2OAuCl]^+, 631$ $[C_{30}H_{30}N_2OAu]^+$, 435 $[C_{30}H_{31}N_2O]^+$. $C_{30}H_{30}AuClN_2O$ (667.00): calcd. C 54.82, H 4.53, N 4.02; found C 54.86, H 4.41, N 3.88.

Gold(III) Complex 6: Compound **5** (100 mg, 0.15 mmol) was dissolved in dcm (5 mL) and the solution cooled to -50 °C (2-propanol/liquid nitrogen). A solution of Br₂ in dcm (0.25 mL of a 0.623 M Br₂ solution, 0.16 mmol) was added whilst stirring. Subsequently the reaction mixture turned red. The solution was slowly allowed to warm to room temperature over 4 h. The solvent was removed under reduced pressure and the residue re-crystallized

Pages: 10

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from dcm/diethyl ether to yield a red powder. Slow gas-phase diffusion of diethyl ether into a dilute chloroform solution gave bright-red crystals suitable for X-ray diffraction, yield 100 mg (80%). ¹H NMR (300 MHz, CDCl₃, 30 °C): $\delta = 7.52-7.47$ (m, 2 H), 7.38–7.29 (m, 4 H), 7.24 (m, 2 H), 7.21–7.14 (m, 6 H), 5.71 (s, 2 H, O-CH₂), 2.59 [sept, J_{HH} = 6.7 Hz, 2 H, CH(CH₃)₂], 1.38 [d, J_{HH} = 6.7 Hz, 6 H, CH(CH₃)₂], 1.04 [d, J_{HH} = 6.7 Hz, 6 H,

CH(CH_{3})₂] ppm. ¹³C NMR (75 MHz, CDCl₃, 30 °C): δ = 148.1, 145.2, 136.7, 135.0, 133.0, 131.6, 130.7, 127.6, 127.5, 127.0, 126.8, 126.7, 126.3, 123.5, 122.2, 120.4, 117.9, 114.9, 113.7, 69.8, 28.0, 25.7, 22.1 ppm. MS (ESI pos): m/z = 1343 [(LAu)₂Br]⁺, 1297 [(LAu)₂Cl]⁺, 631 [C₃₀H₃₀N₂OAu]⁺. C₃₀H₃₀AuBr₂ClN₂O·CHCl₃ (946.19): calcd. C 39.35, H 3.30, N 2.96; found C 39.73, H 3.08, N 2.76.

Supporting Information (see footnote on the first page of this article): Emission spectrum of neat **5** at 298 K and emission decay of neat **5** and of **5** and **6** in ethanol glass at 77 K.

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Charles V. Wee V. Charles C. M. Charles Charles

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NHC Gold Complexes

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Synthesis, Characterization and Luminescence of Gold Complexes Bearing an NHC Ligand Based on the Imidazo[1,5-*a*]quinolinol Scaffold

Keywords: Nitrogen heterocycles / Carbenes / Gold / Silver / Luminescence



Silver(I), gold(I) and gold(III) complexes bearing an NHC ligand based on imidazo[1,5-a]quinolinol have been synthesized. The molecular structures of the gold complexes reveal distortion of the rigid NHC moiety due to steric repulsion between the gold and oxygen atoms. At room temperature, the complexes are weakly fluorescent, whereas at 77 K the emission spectra are dominated by phosphorescence.